PB-242 547

ENGINEERING AND COST STUDY OF AIR POLLUTION CONTROL FOR THE PETROCHEMICAL INDUSTRY VOLUME 5: FORMALDEHYDE MANUFACTURE WITH THE MIXED OXIDE CATALYST PROCESS

R. B. Morris, et al

Air Products and Chemicals, Incorporated
Marcus Hook, Pennsylvania

March 1975

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U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Waste Management
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

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ENGINEERING AND COST STUDY OF AIR POLLUTION CONTROL FOR THE PETROCHEMICAL INDUSTRY VOLUME 5: FORMALDEHYDE MANUFACTURE WITH THE MIXED OXIDE CATALYST PROCESS

by

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March 1975

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PETROCHEMICAL AIR POLLUTION STUDY

INTRODUCTION TO SERIES

This document is one of a series prepared for the Environmental Protection Agency (EPA) to assist it in determining those petrochemical processes for which standards should be promulgated. A total of nine petrochemicals produced by 12 distinctly different processes has been selected for this type of in-depth study. These processes are considered to be ones which might warrant standards as a result of their impact on air quality. Ten volumes, entitled Engineering and Cost Study of Air Pollution Control for the Petrochemical Industry (EPA-450/3-73-006a through j) have been prepared.

A combination of expert knowledge and an industry survey was used to select these processes. The industry survey has been published separately in a series of four volumes entitled Survey Reports on Atmospheric Emissions from the Petrochemical Industry (EPA-450/3-73-005a, b, c and d).

The ten volumes of this series report on carbon black, acrylonitrile, ethylene dichloride, phthalic anhydride (two processes in a single volume), formaldehyde (two processes in two volumes), ethylene oxide (two processes in a single volume) high density polyethylene, polyvinyl chloride and vinyl chloride monomer.

ACKNOWLEDGEMENTS

The study reported in this volume, by its nature, relied on the fullest cooperation of the companies engaged in the production of formaldehyde. Had their inputs been withheld, or valueless, the study would not have been possible or at least not as extensive as here reported. Hence, Air Products wishes to acknowledge this cooperation by listing the contributing companies.

Allied Chemical Corporation
Borden Chemical Company
Celanese Corporation
E. I. duPont deNemours & Company
GAF Corporation
Georgia Pacific Corporation
Gulf Oil Corporation
Hercules, Inc.
Hooker Chemical Company
Monsanto Company
Reichhold Chemical Company
Tenneco Chemical Company
Wright Chemical Company

Additionally, Air Products wishes to acknowledge the cooperation of the member companies of the U. S. Petrochemical Industry and the Manufacturing Chemists Association for their participation in the public review of an early draft of this document. More specifically, the individuals who served on the EPA's Industry Advisory Committee are to be commended for their advice and guidance at these public meetings.

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SUMMARY

The formaldehyde industry has been studied to determine the extent of air pollution resulting from the operations of the various plants and processes of the industry. The purpose of the work was to provide the Environmental Protection Agency with a portion of the basic data required in order to reach a decision on the need to promulgate air emission standards for the industry.

It was concluded that there are two basic processes for the production of formaldehyde. They both utilize methanol as a raw material in an air oxidation process. Neither appears to have any significant advantage which would alter its relative growth rate. A third process, utilizing partial oxidation of light hydrocarbons to produce formaldehyde appears to be obsolete. The principal differences between the two methanol based processes are the catalyst and the methanol/air ratio. The subject of this report is the process utilizing a mixed metal oxide catalyst and a methanol lean feed mixture with air. A separate study devotes itself to the other process which uses a silver catalyst and a methanol rich feed mixture with air. (Report Number EPA-450/3-73-006d.)

In general terms, the air emissions from the mixed oxide catalyst process fall into the categories of hydrocarbons (formaldehyde, dimethyl ether and methanol) and carbon monoxide. As practiced today, virtually no oxides of nitrogen, oxides of sulfur or particulates are emitted from the process. The process is currently undergoing rather intensive study of techniques for recycling the main vent stream thus reducing emissions and improving processing efficiency. This fact makes it difficult to estimate an emission factor for the process but it probably falls in the range between 0.02 and 0.04 lbs./lb. of 37% formaldehyde produced for recycle and non-recycle operation, respectively. Of these totals, carbon monoxide account for about 0.016 lbs./lb. of 37% formaldehyde, regardless of the recycling operation. The balance is hydrocarbon emission, about half of which is formaldehyde and one-third dimethyl ether from a non-recycle operation. However, from a recycle operation formaldehyde and dimethyl ether each account for less than one-fourth of the total hydrocarbon emission factor. Based on an approximate median between these extremes it has been estimated that the process emitted about 25 million pounds of hydrocarbons and about 25 million pounds of carbon monoxide into the atmosphere in 1973. If all future mixed oxide process plants are built to incorporate the best present day recycling techniques, it has been estimated that the hydrocarbon emission will increase to just over 32 million pounds per year and the carbon monoxide emissions to about 55 million pounds per year by 1985.

Formaldehyde is normally marketed as a 37-51% water solution. Therefore, all plants have a water scrubber (absorber) on the main process stream before it is vented to the atmosphere (or recycled). Most plants also have a mist eliminator on this stream to minimize the entrainment of water from the absorber. Only one of the plants surveyed has any further emission control equipment and that is an additional water scrubber. It is quite efficient with respect to methanol and formaldehyde but because of the low water solubility of carbon monoxide and dimethyl ether, it does little toward reducing these emissions. Furthermore, it is expensive to install, especially on existing plants and merely transfers a portion of the emission problem from air to water. Consequently, water scrubbing was not adjudged to be the "most feasible" method of emission control although it could certainly be argued that it is the "best demonstrated" technique. However, the available data seem to indicate that the best recycle operations do nearly as well as water scrubbing with

SUMMARY (continued)

respect to air emissions at a lower cost, without transferring the problem to another medium and are thus the best demonstrated technique. The conclusion is evidenced above by the forecast of only a little over seven million pounds per year increase in hydrocarbon emissions by 1985 if recycling operations are employed on all new plants. The major unanswered question is whether or not recycling can be economically incorporated into those existing plants that do not currently operate in this manner.

Since none of the demonstrated techniques reduce carbon monoxide emissions and since uncertainty exists about the universal applicability of recycling techniques, incineration techniques were also studied. It was concluded that though not demonstrated, a thermal incinerator on every existing and new plant would reduce the process emission factor to about 0.001 pounds per pound of 37% formaldehyde which would result in just over three million pounds per year of atmospheric emissions by 1985. This would not cause a significant economic burden for the industry, because at 1973 prices, these incinerators, whether applied to either existing or new model plants of 100 MM lbs./year capacity would cost only about $54,000 each. However, at 1973 fuel prices, this results in nearly $40,000 per plant in total annual operating cost besides being wasteful of fuel. The addition of a heat recovery system on thie incinerator can not be economically justified at 1973 prices even though it would reduce the fuel consumption by about 40 percent. In terms of total industry figures, incinerators without heat recovery would cost about $1,000,000 for existing plants plus an additional $1,000,000 by 1985 (all at 1973 prices) for all new plants. However, this would result in the consumption of about 650 million SCF of natural gas per year by 1985 to achieve an estimated reduction in emissions of 55 million pounds per year of carbon monoxide and 30 million pounds per year of hydrocarbon. In addition, the use of incineration techniques will probably result in the formation of some oxides of nitrogen from the nitrogen present in the normal vent gas.

From the foregoing, it would appear that the major research effort that the formaldehyde industry should make is in the area of improvements in catalysts and improvements in recycle techniques (perhaps through the injection of oxygen to reduce nitrogen recycle). If these types of research can achieve universal applicability of recycle operations along with a reduction in carbon monoxide emissions, it would appear that little or no further air emission control would be required for those producers using the mixed oxide process for formaldehyde production.

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16. ABSTRACT

This document is one of a series prepared for the Environmental Protection Agency (EPA) to assist it in determining those petrochemical processes for which standards should be promulgated. A total of nine petrochemicals produced by twelve distinctly different processes has been selected for this type of in-depth study. Ten volumes, entitled Engineering and Cost Study of Air Pollution Control for the Petrochemical Industry (EPA-450/3-73-006a through j) have been prepared.

A combination of expert knowledge and an industry survey was used to select these processes. The industry survey has been published separately in a series of four volumes entitled Survey Reports on Atmospheric Emissions from the Petrochemical Industry (EPA-450/3-73-005a, b, c, and d).

This volume covers the manufacture of formaldehyde with the mixed oxide catalyst process. Included is a process and industry description, an engineering description of available emission control systems, the cost of these systems, and the financial impact of emission control on the industry. Also presented are suggested air episode procedures and plant inspection procedures.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Air Pollution	Petrochemical Industry	7A
Formaldehyde	Methanol	7B
Carbinols		7C
Hydrocarbons		11G
Carbon Monoxide		13B
Methyl Ether		13H

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I. Introduction

Formaldehyde was first produced in the U. S. in 1901, at that time its chief use was as an embalming agent and disinfectant. Today, some seventy odd years later production capacity exceeds seven and one half billion pounds per year,[5] with approximately two thirds of the production utilized in the formulation of various synthetic resins.

Formaldehyde is normally marketed in aqueous solutions containing from 36 to 50 weight percent formaldehyde. The standard (USP) solution is 37 percent, although large scale industrial users prefer a nominal 50 percent solution. Formaldehyde solutions usually contain sufficient methanol to prevent precipitation of polymer during storage and shipping, although precipitation may be prevented in solutions containing relatively small amounts of methanol by keeping the solution warm.

Formaldehyde is produced principally from methanol. Two processes are dominant in the U. S. today, the mixed oxide catalyzed process and the silver crystal (or gauze) catalyzed process.

The primary licensors of the mixed oxide process are Reichhold and Lummus, while ICI and Borden prevail in the licensing of the silver process. The mixed oxide catalyzed process is the subject of this report.

A third process, based on the partial oxidation of light hydrocarbons, had been utilized by Celanese at their large Bishop, Texas plant until quite recently. That particular facility at Bishop has now been shutdown and replaced by a silver process unit. With national energy source demands escalating feedstock costs for the partial oxidation process, it is extremely doubtful that any new facility in the U. S. will again employ this process.

Atmospheric emissions generated by the mixed oxide catalyst process are associated primarily with the absorber vent gas stream. Minor quantities of hydrocarbons may be discharged from various other sources. Additionally, small quantities of waste water may be produced.

Today an estimated 23% of U. S. formaldehyde capacity is based on the mixed oxide catalyst process. If this process can maintain its present share of the total formaldehyde capacity, it will expand to 3.5×10^9 lbs./year in 1985, from its present 1.73×10^9 lbs./year.

II. Process Description

A. Chemistry

The chemistry of the formation of formaldehyde from methanol, via the mixed (metal) oxide catalyst process may be shown as follows:

$$CH_3OH + \tfrac{1}{2} O_2 \longrightarrow CH_2O + H_2O + 38 \text{ Kcal.}$$

This differs from the classical silver-catalyzed process in that (apparently) no hydrogen is produced, and the methanol molecule itself, rather than the produced hydrogen, is oxidized.

Methanol is mixed with a combination of air and recycle vent gas and then heated to between 220 and 350° F in a steam jacketed vaporizer. The air/recycle gas mixture will normally contain about 10% (vol.) oxygen, but always less than 10.9%. The methanol will normally comprise about 9.5% (vol.) of the total converter feed, although it is limited to about 7% for non-recycle operations. (See Figure FM-1)

The super-heated vapors from the vaporizer pass into the converter, where the oxidation reaction takes place, in a multiplicity of tubes filled with a mixed oxide catalyst, between 650° F and 800° F. The heat of reaction is removed by the circulating Dowtherm fluid surrounding the catalyst tubes and is used to produce steam. The converter effluent gases are cooled from approximately 500° F to about 220° F in a heat exchanger prior to being quenched to near 100° F in the absorber.

The absorber consists of a bubble cap column which may have two water-cooled heat exchangers in the upper portion. The converter effluent vapors are introduced into the bottom section of the column and flow counter-current to the dilution/scrubbing water, which is pumped onto the top tray and flows downward through the tower. The formaldehyde vapors are absorbed by the water, forming a 37 to 53% solution. This exits from the bottom of the tower. The non-condensibles are vented from the top of the absorber where part is recycled and part goes directly to the atmosphere.

B. Recycle Operation

In 1948, du Pont discovered [18] that if the volume percent of oxygen in the gas employed for the oxidation (i.e., air plus recycle gas) of methanol is held below 10.9 vol. %, then no explosion will occur no matter how much methanol is added to the mixture. This condition is most easily effected by recycling and mixing the relatively oxygen poor absorber vent gases with the fresh charge air prior to their admixture with the methanol. The advantages resulting from this type of operation are as follows:

(1) Increased capacity.
(2) Higher yield.
(3) Increased safety.
(4) Lower emissions.

Today nearly all mixed-oxide catalyst plants utilize this mode of operation.

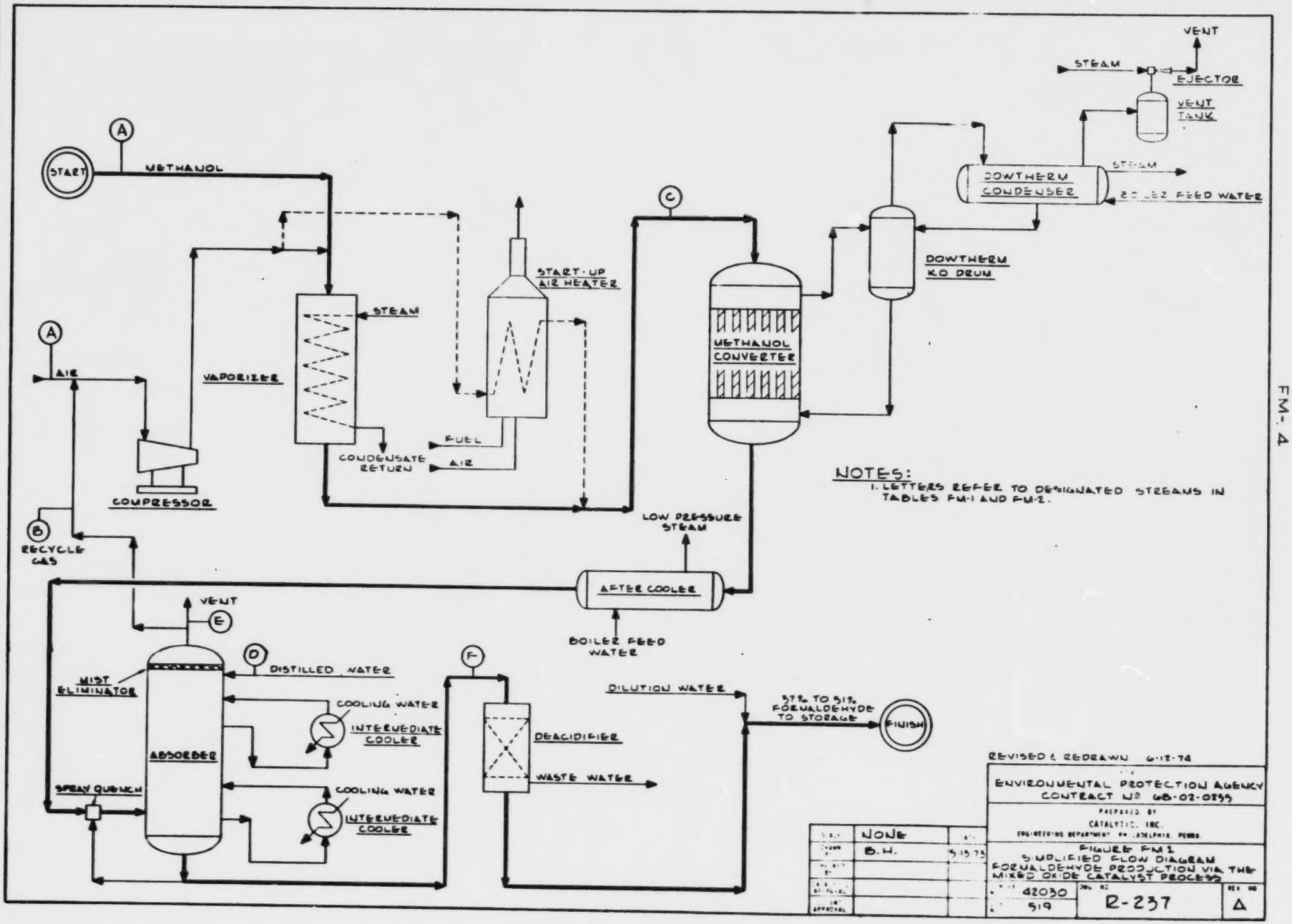
C. Material Balance

Table FM-1 presents a typical material balance for mixed oxide catalyst process formaldehyde production. Absorber vent gas composition is based on data furnished by questionnaire respondents-at what are presumed to be typical vent gas recycle rates. Yields, etc., are based on a combination of questionnaire and published data and are shown below:

	Mole %
Total Converter Feed	
Methanol	$\sim$ 10
Oxygen	$<$ 10.9
Recycle Gas	
Ratio	Not Specified
Oxygen	8
Methanol Conversion	98
Formaldehyde Yield	94

Table FM-1 material balance relates to an average size plant (100 MM lbs./year of 37% formaldehyde). This typical unit will be used in economic studies discussed later in this report. Table FM-2 presents the same material balance with quantities expressed as tons per ton of 37% formaldehyde.

Table FM-3 presents an estimated heat balance around the converter section.



NOTES:
1. LETTERS REFER TO DESIGNATED STREAMS IN TABLES FM-1 AND FM-2.

FM-4

REVISED & REDRAWN 6-12-74

	NONE	
	B.H.	5-15-75

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FIGURE FM-1
SIMPLIFIED FLOW DIAGRAM
FORMALDEHYDE PRODUCTION VIA THE
MIXED OXIDE CATALYST PROCESS

42030		E-237	Δ
519			

TABLE FM-1
TYPICAL MATERIAL BALANCE FOR MIXED OXIDE CATALYST PROCESS FORMALDEHYDE PLANT PRODUCING 100 MM LBS./YR. OF 37% FORMALDEHYDE

	Fresh Feed	Recycle Absorber Gas	Total Feed	Absorber 'Make-Up' Water	Absorber Vent Gas	Absorber Bottoms (Product)*
Stream I. D.	A	B	C	D	E	F
Formaldehyde		Composition may be calculated as follows: ** "B" = (PR / (100 - PR)) x "E"	Composition equals column "A" plus column "B"		5	4,534
Methanol	5,121				21	61
Dimethyl Ether					10	
Nitrogen	12,994				12,994	
Oxygen	3,944				1,336	
Carbon Dioxide	7				22	
Carbon Monoxide					151	
Water				5,156	429	7,660
Total - Lbs./Hr.	22,066			5,156	14,968	12,255

*May include small amount of formic acid.

**% recycle (P.R.) = $\frac{\text{moles of recycle}}{\text{moles of recycle + moles of vent}}$ x 100 (normal range - 0 to 90%)

TABLE FM-2
TYPICAL MATERIAL BALANCE FOR
MIXED OXIDE CATALYST PROCESS FORMALDEHYDE PLANT

UNITS - TON/TON OF 37% FORMALDEHYDE

Stream I. D.	Fresh Feed	Recycle Absorber Gas	Total Feed	Absorber Make-Up Water	Absorber Vent Gas	Absorber Bottoms (Product)*
	A	B	C	D	E	F
Formaldehyde		Composition may be calculated as follows:** "B" = $\left(\frac{PR}{(100 - PR)}\right)$ x "E"	Composition equals column "A" plus column "B"		.0004	.3700
Methanol	.4179				.0017	.0050
Dimethyl Ether					.0008	
Nitrogen	1.0603				1.0603	
Oxygen	.3218				.1090	
Carbon Dioxide	.0006				.0018	
Carbon Monoxide					.0123	
Water				.4207	.0350	.6250
Total	1.8006			.4207	1.2213	1.0000

*May include small amount of formic acid.

**% recycle (P.R.) = $\frac{\text{moles of recycle}}{\text{moles of recycle + moles of vent}}$ x 100 (normal range = 0 - 90%)

TABLE FM-3
FORMALDEHYDE PRODUCTION
VIA
MIXED OXIDE CATALYST PROCESS

GROSS HEAT BALANCE - CONVERTER SECTION ONLY (1)

Heat In	BTU/Lb. of 37% HCHO
Charge vaporizer/heater	558
Exothermic heat of reaction	878
Total	1436

Heat Out	
Converter temperature control (2)	700
After cooler (3)	336
Quench and residual enthalpy (4)	400
Total	1436

NOTES:

(1) Based on Table FM-2 Material Balance.
(2) Converter maximum temperature @ 750° F and outlet @ 500° F.
(3) Outlet @ 200° F.
(4) Base temperature is 60° F.

III. Manufacturing Plants and Emissions

Table FM-4 presents a list of U. S. plants producing formaldehyde. Production via the mixed oxide catalyst process is used by nine producers in a total of eighteen different plants. The greatest number of plants (eight), are located in the Southeast. Five are located in the Pacific Northwest, three in New Jersey and one each in Ohio and Texas. The plants range in capacity from 40 to 160 MM lbs./year of 37% formaldehyde.

Table FM-5 shows individual plant capacity figures and atmospheric emission data for the various formaldehyde plants surveyed in this study. The plants in the tabulation include both the smallest and largest plants currently on-stream, and represent 40% of the total U. S. installed mixed oxide catalyst process capacity. Emissions from these plants are reported to be as follows:

A. Continuous Air Emissions

1. Absorber Vent

The emissions from this vent constitute the primary source of air pollution associated with the production of formaldehyde. Indeed, one respondent reports it as the sole source of his emissions.

The composition of the absorber vent gas stream is dependent on many variables, some of which are:

(a) Recycle ratio.
(b) Strength of formaldehyde produced.
(c) Catalyst formulation.
(d) Catalyst age.
(e) Absorber temperature.

The variable which probably has the single greatest effect on emissions is the gas recycle ratio. The importance of this parameter may be seen in the following comparison of absorber vent gas composition for recycle [a] and non-recycle operations:

	Emissions [e] Lb./Lb. of 37% HCHO	
Components	Recycle Operation [b]	Non-Recycle Operation [c]
Nitrogen	1.1735	4.2918 (d)
Oxygen	.0932	1.0772 (d)
Carbon Dioxide	.0018 (d)	).0182 (d)
Carbon Monoxide	.0170	)
Methanol	.0020	.0034 (d)
Formaldehyde	.0008	.0092
Dimethyl Ether	.0008 (d)	.0070
Total Hydrocarbons	.0036	.0196

(a) Recycle ratio is unknown (but assumed typical).
(b) Average of data from plants 14-21 and 14-22.
(c) Average of data from plants 14-16 and 14-19.
(d) Single data source.
(e) See Table FM-6 for more complete emission summary.

TABLE FM-4
SUMMARY OF U. S. FORMALDEHYDE PLANTS Sheet 1 of 2

NOTE: The following tabulation of formaldehyde producers indicates published production capacity (MM lbs./year) by company, location and process. Determination of the process utilized was by combination of published information, questionnaire responses and private communications.

Company	Location	Silver Process	Metal Oxide Process
Allied	Ironton, Ohio	308	
Borden			
	Demopolis, Ala.	80	
	Diboll, Texas	70	
	Fayetteville, N. C.	200	
	Fremont, Calif.	80	
	Kent, Wash.	70	
	La Grande, Oregon	40	
	Louisville, Ky.	70	
	Missoula, Mont.	80	
	Sheboygan, Wisc.	120	
	Springfield Oregon	260	
Celanese	Bishop, Texas	1300	
	Newark, N. J.		117
	Rock Hill, S. C.		117
Commercial Solvents	Sterlington, La.	30	
	Seiple, Pa.	80	
Du Pont	Belle, W. Va.	485	
	Grasselli, N. J.	150	
	Healing Spring, N. C.	200	
	La Porte, Texas	200	
	Toledo, Ohio	320	
	Linden, N. J.	150	
GAF	Calvert City, Ky.		100
Georgia Pacific	Columbus, Ohio		100
	Coos Bay, Oregon		80
	Crosett, Ark.	100	60
	Albany, Oregon		100
	Taylorsville Miss.		100
	Vienna, Ga.	100	
Gulf	Vicksburg, Miss.		40
Hercules	Louisiana, Mo.	170	
	Wilmington, N. C.	95	
Hooker	N. Tonawanda, N. Y.	135	
Monsanto	Alvin, Texas	150	
	Addyston, Ohio	110	
	Eugene, Oregon	100	
	Springfield, Mass.	280	

TABLE FM-4 CONTINUED
SUMMARY OF U.S. FORMALDEHYDE PLANTS

Sheet 2 of 2

Company	Location	Silver Process	Metal Oxide Process
Reichhold	Hampton, S.C.	36	
	Houston, Texas		100
	Moncure, N.C.		100
	Tacoma, Wash.		40
	Tuscaloosa, Ala.	70	
	Kansas City, Kansas	40	
	White City, Oregon		50
	Malvern, Ark.		100
Rohm & Haas	Philadelphia, Pa.	25	
Skelly	Springfield, Oregon		70
	Winfield, La.		70
Tenneco	Fords, N.J.	105	160
	Garfield, N.J.	105	
Union Carbide	Bound Brook, N.J.		150
Wright	Acme, N.C.		75
Total Process Capacity - MM Lbs./Year		5,914	1,729*
Number of Plants		35	19
Average Plant Size - MM Lbs./Year		169	91
Capacity of Total Industry - MM Lbs./Year		7,643	
Percent of Total Industry Capacity		77.4	22.6

*Most recent total reported

TABLE FM-5
NATIONAL EMISSIONS INVENTORY
FOR
FORMALDEHYDE PRODUCTION
VIA
MIXED OXIDE CATALYST PROCESS

Plant EPA Code No.	14-2		14-16		14-17	
Capacity - Tons of 37% Formaldehyde/Yr.	30,000		20,000		50,000	
Range in Production - % of Max.	0		18.5		33.3	
Emissions to Atmosphere						
Stream	Absorber Vent	Dowtherm Vent	Absorber Vent	Tank Vent	Compressor Exhaust	Absorber Vent
Flow - Lbs./Hr.	Not Specified	Not Specified	27,619	"Very Small"	Not Specified	Not Specified
Flow Characteristic, Continuous or Intermittent if Intermittent - Hrs./Yr. Flow	Continuous		Continuous		Intermittent?	Continuous
Composition, Tons/Ton of 37% Formaldehyde						
Methanol	+					
Formaldehyde	+		)	+		
Dimethylether	+		).01630			
Nitrogen			4.29180		+	+
Oxygen			1.07720		+	+
Carbon Dioxide			)			
Carbon Monoxide			).01820		+	+
Water			.12030		+	+
Dowtherm		+				
Catalyst Dust						
Vent Stacks	Yes		Yes	Yes	Yes	Yes
Number	1		1	1	1	1
Height - Feet	49		60	49.5	20	73
Diameter - Inches	131		24	6	8	30
Exit Gas Temp. - F°			70-95	< 150	210	50-55
SCFM/Stack			6000-8000	Unknown		
Emission Control Devices	None	None	None	None	None	Yes (FM-1)
Incinerator						
Scrubber						
Other						Mist Elim.
Analysis						
Date or Frequency of Sampling	Never		Infrequent	Never	Never	Never
Sample Tap Location			At Stack			
Type of Analysis	Design Values		GLC and Design			
Odor Problem	No		Yes	Yes	No	
Summary of Air Pollutants (T/T of 37% HCHO)	Cannot be determined				Cannot be determined	
Hydrocarbons			) .01630			
Aerosols & Particulates			+			
NO_x						
SO_x						
CO			+			
Type of Operation - Recycle (R) or Non-Recycle (N.R.)	N.R.		N.R.		R	

FM-11

TABLE FM-5

NATIONAL EMISSIONS INVENTORY

FOR

FORMALDEHYDE PRODUCTION

VIA

MIXED OXIDE CATALYST PROCESS

Plant EPA Code No.	14-19		14-21 and/or 14-23 (1)			14-22
Capacity - Tons of 37% Formaldehyde/Yr.	49,500		50,000 @			50,000
Range in Production - % of Max.	0		0			0
Emissions to Atmosphere						
Stream	Absorber Vent	Tank Vent	Absorber Vent	Dowtherm Vent	Converter Cat. Activ Vent	Absorber Vent
Flow - Lbs./Hr.	73,078	0.07	17.583			14,000
Flow Characteristic, Continuous or Intermittent if Intermittent - Hrs./Yr. Flow	Continuous	Continuous	Continucus	Continuous	Intermittent	Continuous
Composition, Tons/Ton of 37% Formaldehyde						
Methanol	.00055		.00167			.00224
Formaldehyde	.00026	<.00001	.00047			.00112
Dimethylether	.00692		.00084			
Nitrogen	)		1.35081		+	.99624
Oxygen	) 6.21413		.10912		+	.07728
Carbon Dioxide	)		.00177		+	
Carbon Monoxide			.01228		TR	.02160
Water						.03752
Dowtherm				+		
Catalyst Dust					+	
Vent Stacks	Yes	Yes	Yes	Yes	Yes	Yes
Number	1	1	1	1	1	1
Height - Feet	85	8	74	40	42	10
Diameter - Inches	24	4	30	1	14	14
Exit Gas Temp. - F°	80	100	80	80	100-700	92
SCFM/Stack	16,000	1.7	3932	"Nil"	8000	3199
Emission Control Devices	Yes (FM-2)	Yes (FM-3)	None	None	None	Yes (FM-4)
Incinerator						
Scrubber	+	+				
Other						Demister
Analysis						
Date or Frequency of Sampling	10 times (1969)	Never	Never	Never	Never	Twice
Sample Tap Location	At Stack					
Type of Analysis	GLC	Calc'd.	Calc'd.			Date ex design
Odor Problem	No	No	No	No	No	No
Summary of Air Pollutants (T/T of 37% HCHO)						
Hydrocarbons	.00773		.00298			.00336
Aerosols & Particulates			+			
NO_x						
SO_x						
CO			.01228			.02160
Type of Operation - Recycle (R) or Non-Recycle (N.R.)	N.R.		R			R

(1) Questionnaire responses from plants 14-21 and 14-23 were identical.

TABLE FM-6
TYPICAL ABSORBER VENT GAS COMPOSITION
FOR
100 MM LB./YR. (1) FORMALDEHYDE PLANT
MIXED OXIDE CATALYST PROCESS

Normal Range in Composition

Component	Non-Recycle Operation Vol. % (2)	Recycle Operation Vol. % (3)	Typical Flow Rate & Composition Recycle Operation MPH	LB./HR.
Formaldehyde	.01 to 1.0	.03 to .15	0.2	5
Methanol	0 to .7	.05 to .2	0.6	21
Dimethyl Ether	.05 to 2.5	0 to .53	0.2	10
Oxygen	18.5 to 19.6	5.3 to 18.1	41.7	1336
Nitrogen	75.1 to 77.0	73.9 to 89.2 (4)	463.7	12994
Carbon Dioxide		.03 to .09	0.5	22
Carbon Monoxide	2.2 to .4	.28 to 1.9	5.4	151
Water	0.7 to 2.24 (4)	5.1	23.8	429
Totals			536.1	14968

NOTES:

(1) Of 37% formaldehyde.
(2) Basis - questionnaire 14-16, 14-19, 14-22.
(3) Basis - questionnaires 14-23, 14-21.
(4) Calculated by difference.

2. Dowtherm System Vent

Respondents 14-21 and 14-23 report emitting small quantities of Dowtherm vapors to the atmosphere. The quantities are stated to be less than one CFM (which on a lb./lb. basis is <.0020) and normally nil. Respondent 14-2 depicts a similar vent on his flow sheet, but gives no further information. It is believed that most operators maintain similar vents and that at least some of the vent systems include vacuum ejectors. A summary of these data are shown in Table FM-5.

3. Storage Tank Vents

Three of the seven questionnaire respondents report the employment of control devices on at least some of their storage tanks. The majority of the storage tanks associated with the respondents's formaldehyde facilities, however, vent directly to the atmosphere. Never-the-less, emissions from this source are quite low. The operator of plant 14-22 estimates that the emissions from his storage tanks, which employ no vapor conservation devices, total .04 SCFM. Calculated as methanol this amounts to approximately .00002 lbs./lb. of 37% formaldehyde.

B. Intermittent Air Emissions

1. Catalyst Activation Vent

Plants 14-21 and 14-23 report a catalyst activation procedure which results in venting relatively large quantities of N_2, O_2 and CO_2 to the atmosphere about once a year. (Probably for a period of about 24 hours.) These gases may contain trace amounts of ammonium chloride and catalyst dust. However, due to the infrequency of the operation and the low concentration of contaminants, pollution from this source would appear to be negligible. Presumably all operators employ similar procedures.

2. Compressor "Exhaust"

The operator of plant 14-17 is the only respondent reporting atmospheric emissions from this source. The purpose of the vent is not readily apparent nor is it quite clear whether or not there is a continuous discharge from this point. The operator states "normal composition is nearly 100% CO, air and H_2O. During upset conditions, which may last for 20 - 30 minutes, contaminants may leave this source". It would appear from the flow diagram that, for practical purposes, this stream could be considered as part of the absorber vent stream. Other details are summarized in Table FM-5.

C. Continuous Liquid Wastes

The production of various waste water streams has been reported as follows:

Plant 14-2 - "steam drum water".

Plant 14-16 - 8,000 gallons of waste water per day delivered to city sewer.

Plant 14-17 - 1.1×10^6 GPD cooling water circulated with discharge (quantity unspecified) treated on-site.

Plant 14-19 - 2,000 GPH of waste water neutralized and solids removed prior to discharge to county sewage treatment plant.

Plant 14-21 and 14-23 - Both report producing and treating 14,546 gallons of waste water per day (each). This contains: 260 to 550 lb./day HCHO
855 lb./day $Na_2 CO_3$
285 lb./day CHOOH as sodium salt

Plant 14-22 - Reports no waste water.

D. Intermittent Liquid Wastes

No intermittent liquid wastes were reported. It must be assumed, therefore, that the waste liquid stream produced during the regeneration of the ion exchanger resins is included in the report of total liquid wastes. This assumption is corroborated, in part, by the indicated contained salts in plants 14-21 and 14-23 waste water (see above).

E. Solid Wastes

With the exception of one plant, all questionnaire respondents report no solid waste production. Plant 14-16 reports "theoretically no solid material is produced. Actually solid paraformaldehyde must sometimes be cleaned from absorber sump and tank bottoms. In the last year, an estimated 40,000 lbs. has been flushed to sludge pond on company property where it has been biodegraded. Planned improvements should drastically reduce amount of para formed".

F. Odors

Of the seven questionnaire respondents, two (plants 14-16 and 14-17) reported having received a community odor complaint within the past year. All other plants reported detecting odors (usually formaldehyde), at least occasionally, on-site.

G. Fugitive Emissions

Three plants offered estimates of fugitive emissions (generally exclusive of tank vents, which were reported separately). They are:

Plant	Fugitive Emissions Lb./Lb. of 37% HCHO
14-17	.001
14-21	.0005
14-23	.0005

IV. Emission Control Devices and Systems

A. Overview

The industry-wide acceptance and utilization of vent gas recycling techniques has resulted in a major reduction (see Section III-A) of typical mixed oxide plant emissions. The ensuing discussion of control devices is based on the assumption that these devices will augment that reduction in emissions. In practice, the devices will most probably be more beneficial during those periods when the plant is in a non-recycle mode or has not yet achieved optimum recycle conditions. However, for the purpose of this report, device sizing, costing, associated material balances, etc., will relate to emission control devices designed primarily for normal recycle conditions.

B. Devices Currently Employed

It would appear that - based on the information supplied in the returned questionnaires - the majority of U.S. plants do not employ emission control devices. Plants 14-17 and 14-22 both reported the use of mist eliminators in the tops of their absorbers. Sufficient data to estimate the efficiency of these devices were lacking. (See Table FM-7)

The only major emission control system reported is respondent 14-19's water scrubbing facility. Both absorber vent gases and storage tank vents are water scrubbed prior to discharge to the atmosphere. The indicated efficiency of the absorber scrubber is 66 to 67%, whereas the tank vent device is estimated to be about 99% efficient. (The difference in efficiency being due to the presence of the dimethyl ether in the absorber vent gas stream, which, relative to formaldehyde and methanol, is water insoluble.)

C. Feasible Devices - Not Currently Employed

1. Combustion Devices

With few exceptions, the devices that are most efficient in removing carbon monoxide and contained hydrocarbons from the typical formaldehyde vent stream shown in Table FM-6, are those utilizing combustion. For the subject process, for these devices, investment costs are lower and operating costs higher than for other devices evaluated. The relatively high operating costs are attributable to the fact that supplemental fuel must be provided to support combustion since the heat available from the combustion of the contained pollutants is less than one MM BTU/Hr.

(a) Thermal Incinerator

Table FM-8 presents a material balance for this type of control device. The data in the table are based on a 1500° F combustion zone temperature and four mole % oxygen in the stack gas (exclusive of the oxygen supplied by the absorber vent). This should assure complete combustion of all pollutants.

Although there are no known tail gas incinerators employed in the subject service, information available from similar installations indicates that combustion efficiency should be quite high, 99+%.

TABLE FM-7
CATALOG OF EMISSION CONTROL DEVICES
FORMALDEHYDE VIA THE MIXED OXIDE CATALYST PROCESS

ABSORBER/SCRUBBER/MIST ELIMINATOR				
EPA Code No. for plant using	14-17	14-19	14-19	14-22
Flow Diagram (Fig. I) Stream I. D.	E	E		E
Device I. D. No.	FM-1	FM-2	FM-3	FM-4
Control Emission of	HCHO & CH_3OH	HCHO	HCHO & CH_3OH	HCHO & CH_3OH
Scrubbing/Absorbing Liquid	None	Water	Water	None
Type - Spray				
Packed Column				
Column w/trays		X		
Number of trays		4		
Tray type				
Other	Mist Elimin.		Seal Tank	"Centrifix" L.P. Lime Seperator
Scrubbing/Absorbing Liquid Rate - GPM	0	24	20	0
Design Temperature (Operating Temp.) - F°	Not Specified	(80)	(100)	(92)
Gas Rate, SCFM (lb./hr.)		16,000	1.7	3,199
T-T Height, Ft.		6.5		
Diameter, Ft.				
Washed Gases to Stack		Yes	Yes	Yes
Stack Height - Ft.		85	8	10
Stack Diameter - Inches		24	4	14
Installed Cost - Mat'l. & Labor - $		52,500	10,000	4,000
Installed Cost based on - "year" - dollars		1968	1967	1966 - 1971
Installed Cost - c/lb. of 37% HCHO - Yr.		.0530	.0101	.0040
Operating Cost - Annual - $ - 1972		8,000	200	0
Value of Recovered Product, $/Yr.		0	0	0
Net Operating Cost - Annual - $		8,000	200	0
Net Operating Cost - c/lb. of 37% HCHO		.0081	.0002	0
Efficiency - % - SE*		67	~99	--
Efficiency - % - SERR*		66	~99	--

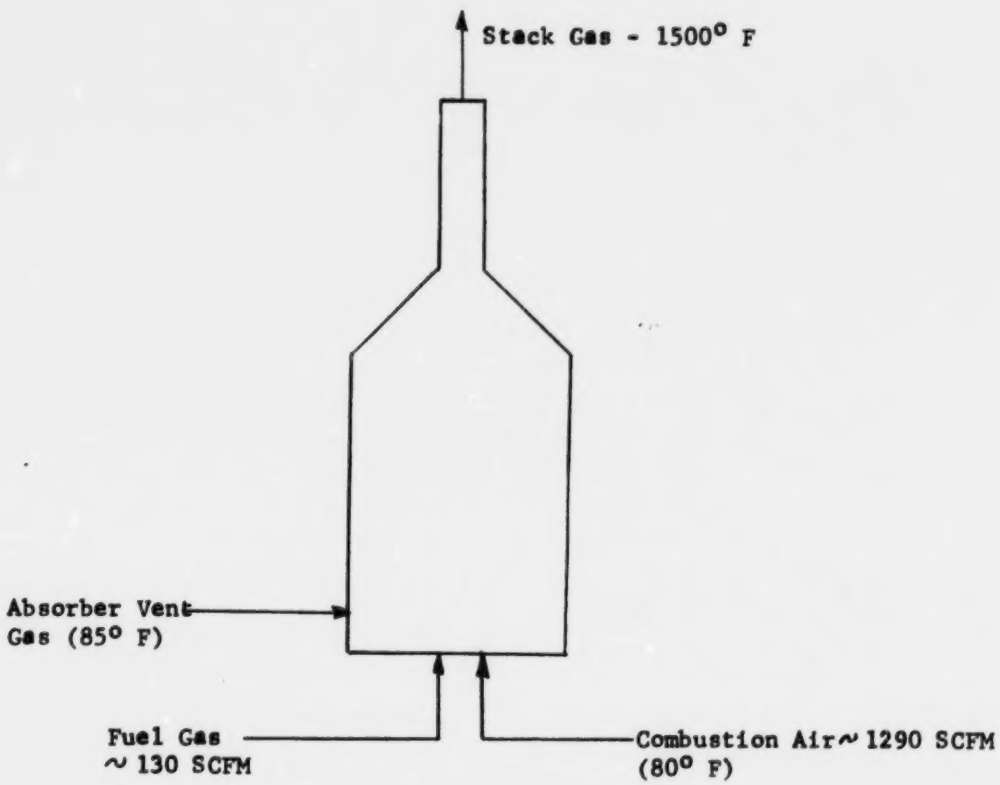
*See Appendix III for explanation and definition of these items.

TABLE FM-8
THERMAL INCINERATOR
100 MM LB./YR. FORMALDEHYDE PLANT
ABSORBER VENT STREAM

OVERALL MATERIAL BALANCE - LB./HR (1)

Component	Absorber Vent Gas	Fuel Gas	Combustion Air	Flue Gas (2)
Formaldehyde	5			
Methanol	21			
Dimethyl Ether	10			
Oxygen	1,336		1,356	1,252
Nitrogen	12,994		4,493	17,487
Carbon Dioxide	22			1,215
Carbon Monoxide	151			
Water	429			1,191
Methane		328		
Total	14,968	328	5,849	21,145

(1) Based on recycle operation.
(2) Excludes any conversion of atmospheric nitrogen to NOx.



There are several drawbacks to thermal incinerators, as follows:

(1) Vent gas is available only at low pressure.

(2) Because the HC and CO concentration in the vent gas stream is below the L.E.L., supplemental fuel must be added to sustain combustion.

(3) Due to the relatively small size of the stream, waste heat recovery is not attractive.

(b) Catalytic Incinerator

A conventional catalytic incinerator could reduce pollutants to levels similar to those attainable with a thermal unit (see Table FM-9 for material balance). The catalytic incinerator would operate at lower temperatures (1000° F - 1200° F) and convert less atmospheric nitrogen to NOx. Catalytic incinerator operating costs are expected to be about 25% lower than those projected for a thermal unit, with fuel savings more than off-setting catalyst costs.

(c) Flare System

This control device is defined as one which requires supplemental fuel, as contrasted to a plume burner which has a self supporting flame. Its main other disadvantage is that efficiency for removal of contaminants is less than for other combustion devices. The efficiency will be influenced to some extent by the composition of the vent gas. Based upon qualitative data from similar control devices, it is estimated that 90% of CO and hydrocarbon pollutants will be burned.

2. Water Scrubbers

Table FM-10 presents a material balance for this type of device when used in a recycle type of operation. It should be noted that approximately five times more methanol and formaldehyde will be vented if non-recycle operation is employed. The indicated performance is based on data provided by questionnaire response. A water scrubber will require more capital investment than any of the combustion devices. Scrubbers also have the following performance deviciencies:

(a) Efficiency of removing total hydrocarbons is less than for combustion devices. Efficiency of removing dimethyl ether is essentially zero.

(b) Efficiency of removing carbon monoxide is near zero.

(c) Air contaminants are transferred rather than destroyed and thus require additional treatment or result in water pollution, although partial recycle may be possible, or additional costs may be minimalif the treatment is incremental to an existing system.

TABLE FM-9
CATALYTIC INCINERATOR
100 MM LB./YR. FORMALDEHYDE PLANT
ABSORBER VENT STREAM

OVERALL MATERIAL BALANCE - LB./HR.(1)

Component	Absorber Vent Gas	Fuel Gas	Combustion Air	Flue Gas (2)
Formaldehyde	5			
Methanol	21			
Dimethyl Ether	10			
Oxygen	1,336		860	1,234
Nitrogen	12,994		2,849	15,843
Carbon Dioxide	22			888
Carbon Monoxide	151			
Water	429			920
Methane		208		
Total	14,968	208	3,709	18,885

(1) Based on recycle operation.
(2) Excludes any conversion of atmospheric nitrogen to NOx.

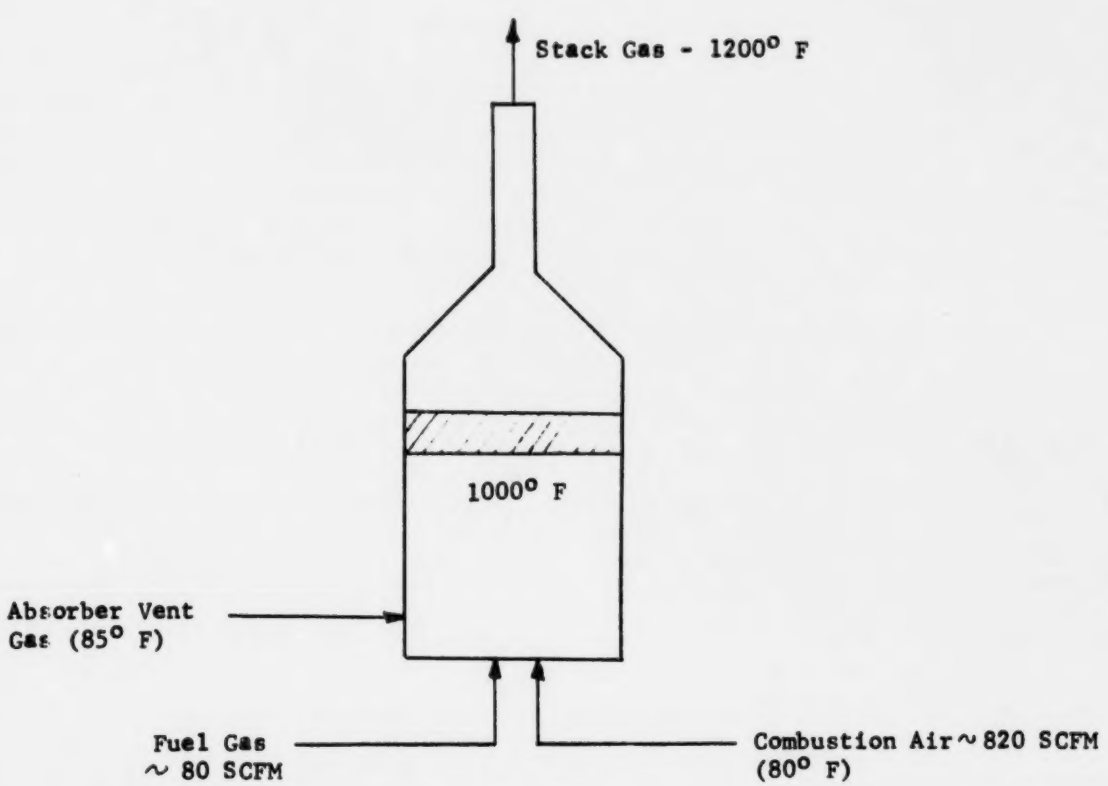
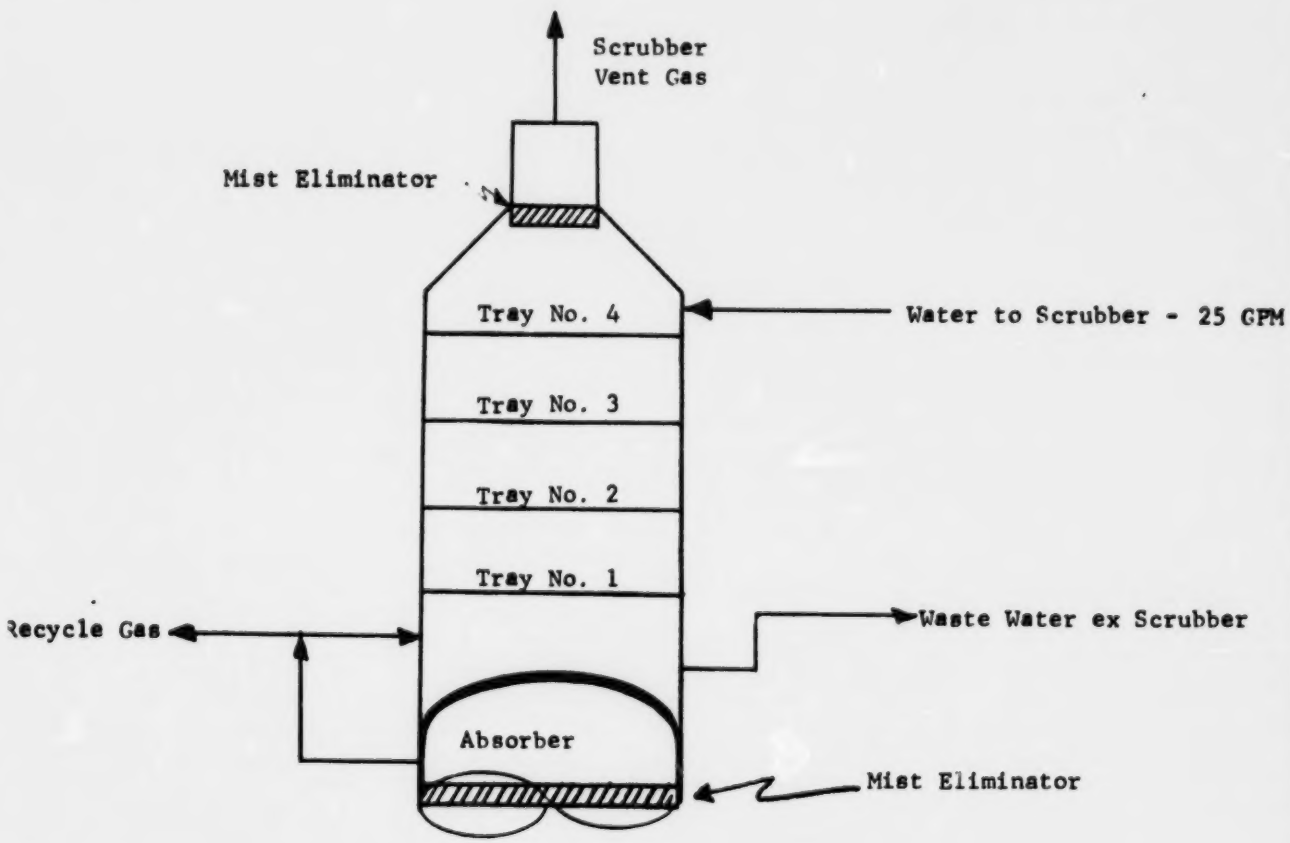


TABLE FM-10
WATER SCRUBBER
FOR
100 MM LB./YR. FORMALDEHYDE PLANT

OVERALL MATERIAL BALANCE - LB./HR.

Component	Absorber Vent Gas	Scrubber Vent Gas	Liquid to Scrubber	Liquid from Scrubber
Formaldehyde*	5	0.6		4.4
Methanol*	21	1.2		19.8
Dimethyl Ether	10	10		0
Nitrogen	12,994	12,994		
Oxygen	1,336	1,336		
Carbon Dioxide	22	22		
Carbon Monoxide	151	151		
Water	429	429	12,500	12,500
	14,968	14,943.8	12,500	12,524.2



*Venting rates will be about five times the levels shown if non-recycle operation is employed.

V. National Emissions Inventory

Because emissions correlate with degree of absorber vent gas recycle and because existing plants utilize varying degrees of recycle, there are various ways of presenting a national emissions inventory. Emissions could be based on:

(1) Average of emissions reported by all respondents and displayed in Table FM-5.

(2) Average emissions based on 'average' recycle plant operation - as shown in the tabular listing in Section III-A-1 (Page FM-8).

(3) Emissions based on best existing recycle operation, which is thought to be typical of future plant emissions - as presented in Table FM-1 and FM-2.

In order to typify current (1973) emissions the first listed basis will be used. (Note that this is not the basis for emission factors, economic data, etc. for future plants listed in other sections of this report. Since these pertain to new or future operations, they accordingly relate to the third listed basis.)

Component	Average Emissions (a) Lb./Lb. of 37% HCHO	Total Emissions (b) MM Lbs./Yr.
Hydrocarbons	0.0149	25.7
CO	0.0144	24.9
	0.0293	50.6

Since formaldehyde production has generally been reported as undergoing no seasonal variation, emissions should be fairly constant throughout the year, unless absorber tower top section cooling capacity is marginal (or does not exist). In that case, emissions will tend to be somewhat higher during warm weather.

(a) Weighted average based on individual plant emission factors and formaldehyde production. (Includes .0005 lbs. HC/lb. of 37% HCHO as fugitive emissions.)
(b) Based on 1729 MM lbs./year mixed oxide catalyst process capacity and assuming production rate equals capacity.

VI. Ground Level Air Quality Determination

A summary of air emissions data from the various surveyed formaldehyde plants has been presented in Table FM-5. This table includes emissions from absorber vent streams and other reported sources. An estimate of fugitive emissions is given in Section III-G of this report.

Table FM-5 provides operating conditions and physical dimensions of the various vent stacks. The EPA will use this information together with the air emission data to calculate ground level concentration for use in subsequent reports.

VII. Cost Effectiveness of Controls

Table FM-11 presents a cost analysis of alternate methods of reducing air pollution related to the emission of absorber vent gases. Economic data presented in this table are for a new plant producing 100 MM lbs./year of 37% formaldehyde via the absorber vent gas recycle mode of operation. The data are based on the following:

A. Investment (1973 Dollars)

1. Incinerators

Published data (14) were used to determine both thermal and catalytic incinerator costs. It should be noted that these are "off-the-shelf" units. Incinerators specially designed for a given application might be considerably more expensive.

2. Flare System

Costs for this device were based on a special flare study as authorized by the EPA's Project Officer on this contract.

3. Scrubbers

Investment data provided in questionnaire responses on both the subject process and other processes were used to determine scrubber costs.

B. Operating Expenses

1. Depreciation - 10 year straight line.

2. Interest - 6% on total capital.

3. Maintenance - If plant survey data were not provided, maintenance was set at 2% of investment, except for catalytic incinerators and water scrubbers, for which the maintenance was set at 4% of investment.

4. Labor - Virtually no operating labor is required for any of the devices listed in Table FM-11. A nominal eight man hours/week was assumed for the water scrubber and catalytic incinerator and four man hours/week labor was assigned to the other devices.

5. Utilities - Unit costs are based on typical value for the Gulf Coast area.

It is judged that all of the devices listed in Table FM-11 will offer acceptable emission control, even the water scrubber with its relatively poor efficiency rating. The water scrubber offers considerably lower operating costs than the other devices. Additionally, future catalyst modifications may inhibit dimethyl ether production and, therefore, permit better scrubber efficiency. On the debit side, the water scrubber requires the highest investment, removes essentially no carbon monoxide and merely transfers pollutants to another media-water, rather than destroying them. However, it may be possible to re-use a portion of this water by recycling it to the absorber. The flare system, while offering the lowest capital investment, results in the highest operating cost, primarily because it also requires the highest supplemental fuel consumption.

TABLE FM-11
COST EFFECTIVENESS FOR ALTERNATE EMISSION CONTROL DEVICES
BASED ON 100 MM LBS./YR. FORMALDEHYDE PRODUCTION

Stream	Absorber Vent Gas				
Type of Emission Control Device	Thermal Incinerator No Heat Recovery	Thermal Incinerator 40% Heat Recovery	Catalytic Incinerator	Flare System	Water Scrubber
Number of Units	1	1	1	1	1
Capacity of each unit - %	100	100	100	100	100
Feed					
Total Flow, Lbs./Hr.			14,968		
SCFM			3,390		
Composition - Lbs./Lb. of 37% HCHO					
Hydrocarbons			.0029		
Particulates					
NOx					
SOx					
Carbon Monoxide			.0123		
Combined Effluent					
Total Flow - Lbs./Hr.	21,145	21,145	18,885	18,885	14,943
SCFM	4,790	4,790	4,270	4,270	3,385
Emission Control (g)					
SE - %					69 (H.C.)
CCR - %	100	100	100	90	
SERR - %	100	100	100	90	65
Investment - $ (f)	(b)	(b)	(b)	(c)	(a)
Purchased Cost	27,000	34,000	17,000		52,000
Installation	27,000	34,000	13,000		39,000
Total Capital	54,000	68,000	30,000	29,000	81,000
Operation Cost - $/Yr.	(b)	(b)	(b)		(a)
Depreciation (10 years)	5,400	6,800	3,000	2,900	8,100
Interest on capital (6%)	3,200	4,100	1,800	1,700	4,900
Maintenance	1,100 (2%)	2,000 (3%)	1,200 (4%)	600 (2%)	3,200 (4%)
Labor @ $4.85/Hr.	1,000	1,000	2,000	1,000	2,000
Utilities					
Power - 1c/KWH	400	400	400		
Fuel - 40c/MM BTU (d)	25,500	15,300	16,000	25,500	
Process Water - 10c/M. Gal.					
Total Utilities	25,900	15,700	16,400	25,500	1,700
Catalyst			2,300		
Total Operation Cost - $/Yr.	36,600	29,600	26,700	31,700	19,900 (e)

(a) Basedon cost provided by formaldehyde producer on similar installation.
(b) Based on afterburner systems study by Shell Development Co. for EPA (Contract EHSD-71-3)
(c) Based on flare cost from previous study.
(d) Escalation of fuel costs could greatly increase the related operation costs.
(e) Excludes water treatment costs.
(f) Based on 1973 dollars.
(g) See Appendix III for explanation and discussion of efficiency ratings.

Thermal incineration of the absorber vent gas stream offers the most effective means of controlling emissions. However, operating costs are relatively high due primarily to the requirement for supplemental fuel - since the combustibles content of the vent gas is well below the L.E.L. and will not support combustion. Unfortunately, the caloric content of even the enriched stream is probably insufficient to warrant the addition of significant heat recovery hardware. A thermal incinerator could be incorporated with either existing or new plants.

The installed cost of a catalytic incinerator (excluding catalyst costs, which are considered as operating costs) is slightly less than that of a comparable thermal incinerator. This results primarily from its lower operating temperature, and the effect thereof on fabrication and installation. Increased maintenance and catalyst charges are more than off-set by reduced supplemental fuel requirements. Emission control capability has been depicted as being comparable to that of thermal devices, although the possibility for catalyst failure through poisoning, etc., always exists.

The economic data presented for the various combustion devices are based on the absorber vent gas composition shown in the individual devices material balance. (FM-8, FM-9)

Variations in combustible content will result in appropriate changes in supplemental fuel costs and will increase or decrease operating costs proportionately.

Costs for installing the various absorber vent pollution control equipment in existing plants would, for the most part, be the same or only slightly higher than the figures shown in Table FM-11. The actual cost differential would depend largely on space availability and location relative to associated process equipment. The single exception is the absorber vent gas water scrubber. The Table FM-11 cost data for this unit are based on a "piggy-back" type close coupled facility. Installation of this type of unit in an existing plant would be impractical. Additionally, a non "piggy-back" type unit would require a vent gas blower to overcome the increased ΔP caused by connecting piping. Thus, investment and operating costs would be higher for installation of this system in an existing plant.

VIII. Source Testing

It is recommended that source sampling be carried out at one of the newer plants, which has been designed for recycle operation, and at a plant utilizing a water scrubbing device. Either of plants 14-21 or 14-23 would seem to be ideal candidates for the source of 'recycle operation samples' while plant 14-19 is the only plant employing a water scrubber. Thus, plant 14-19 and either 14-21 or 14-23 are the recommended sites for source sampling.

Ideally, the sampling program at plant 14-21 or 14-23 will be sufficiently comprehensive to permit correlation of vent gas emissions with recycle ratio and formaldehyde solution strength. The minimum number of sample sets required would be six, at the following approximate combination of conditions:

	Recycle Gas "Ratio"		
	0%	50%*	100%*
HCHO = 37 wt. %	X	X	X
HCHO = 51 wt. %	X	X	X

Sampling at plant 14-19 (currently a non-recycle operation) will require sampling the scrubber inlet and outlet at most probably only one set of conditions - i.e., typical full capacity operation.

*To be interpreted as 50% and 100% of the maximum possible recycle gas ratio.

IX. Industry Growth Projection

Total annual U. S. formaldehyde production is estimated [3,5] to increase to somewhere between 13 and 19 billion pounds per year of 37% solution by 1985. If the mixed oxide process maintains its present share of the market it will account for the production of 3500 million pounds in 1985, see Figure FM-2.

More than half of all formaldehyde produced is consumed by the construction industry. Urea-formaldehyde resins are used as an adhesive in the manufacture of particle board, and consume 25 percent of formaldehyde production. Phenolic resins are used as an adhesive for plywood and consume about 25 percent of production. Melamine resins are used in decorative laminates (kitchen counters, etc.) and consume about 8 percent of total production. Demand in these areas is expected to remain high, if housing starts continue to maintain record levels.

Hexamine (hexamethylene tetramine) has been accounting for about 6 percent of U. S. formaldehyde production the past few years as a result of the use of large quantities of explosives in the Vietnam War. With the withdrawal of U. S. Forces from that area, it is expected that hexamine consumption will drop sharply.

Pentaerythritol (P.E.) accounts for about 7 percent of formaldehyde production. P.E. is used in the manufacture of alkyd resin surface coatings. Consumption is expected to remain fairly steady.

Urea-formaldehyde fertilizers consume about 5 percent of formaldehyde production. Good growth, up to 9 percent/year, is expected for this industry.

Polyacetal resins account for about 8 percent of formaldehyde use. This outlet is expected to maintain a growth rate of 10 percent/year.

Very little formaldehyde is either exported or imported due to the high costs of transporting a water solution. Thus, fluctuations in the general export/import market will not directly affect U. S. formaldehyde production.

The projected increase in formaldehyde production capacity will require the construction of approximately 18 or 19 new 100 MM lbs./year mixed oxide catalyst process plants between 1972 and 1985. This projection is based on the assumption that the mixed oxide process will continue to account for 23% of total formaldehyde capacity. It is doubtful that a resurgence of the partial oxidation or any other third process will develop during this period.

As shown in Table FM-12, methanol costs represent about 50 percent of formaldehyde 'ex works' production costs. Therefore, formaldehyde selling price is greatly influenced by methanol availability. This effect is mitigated to some extent by the fact that the major formaldehyde producers have captive methanol supplies. Methanol prices are currently very low as a result of recent heavy expansions. The long-term outlook for natural gas prices should eventually result in an upturn in methanol prices, but not until methanol production catches up to capacity.

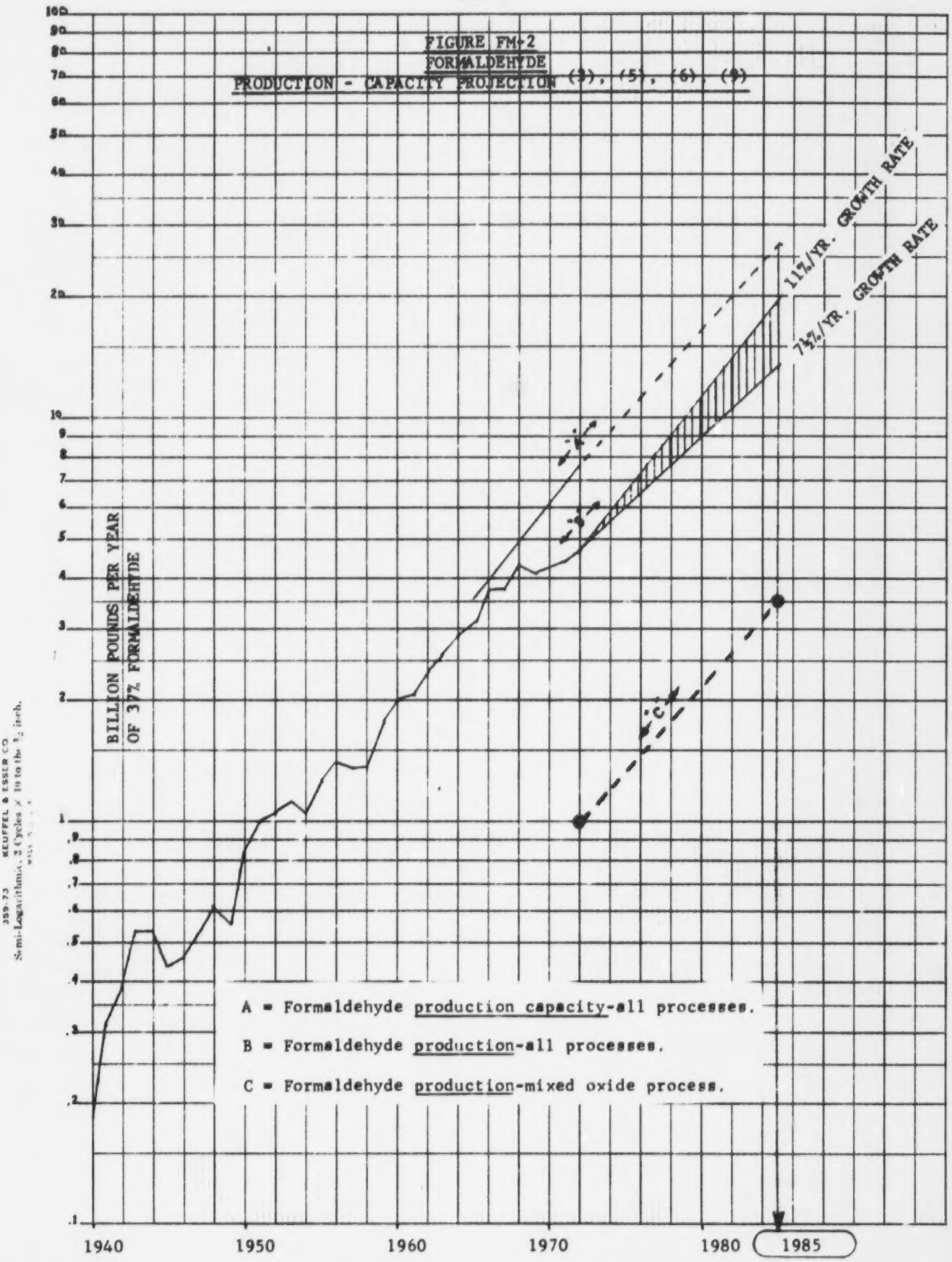


FIGURE FM-2
FORMALDEHYDE
PRODUCTION - CAPACITY PROJECTION (3), (5), (6), (9)
BILLION POUNDS PER YEAR
OF 37% FORMALDEHYDE
11%/YR. GROWTH RATE
7½%/YR. GROWTH RATE
A = Formaldehyde production capacity-all processes.
B = Formaldehyde production-all processes.
C = Formaldehyde production-mixed oxide process.
100
90
80
70
60
50
40
30
20
10
9
8
7
6
5
4
3
2
1
.9
.8
.7
.6
.5
.4
.3
.2
.1
1940
1950
1960
1970
1980
1985
359-73 KEUFFEL & ESSER CO.
Semi-Logarithmic, 3 Cycles x 10 to the 1/2 inch.

X. Plant Inspection Procedures

Plant inspections will be conducted by the appropriate authorities, either on a routine basis or in response to a complaint. The inspecting agent in many cases may have only visual or olifactory observations at his disposal although in some instances, stack monitoring equipment may be available or it might be possible to sample the stack through an accessible sample point.

If the inspector has any reason to suspect that emissions are excessive, some factors that he should consider and/or discuss with plant officials are itemized below:

A. Many plants require seven to ten days to achieve full recycle operation subsequent to start-ups. Pollution control devices may be over-loaded or by-passed during this period. A record should be kept as to when and for how long this occurs. Obviously, an effort should be made to minimize this type of operation. Also, safeguards should be taken to prevent inadvertent opening of control device by-pass valves.

B. Proper operation of the absorber column is necessary to limit emissions from the absorber vent gas in plants with no control device on this stream. When the vent gas is discharged directly to the atmosphere the only practical way hydrocarbon emissions can be controlled is by manipulation of top tower temperatures. Many plants cool the top section of the tower for this purpose. Most plants will keep a record of some or all of the following operating variables and their design limits.

   (1) Process and tower cooling water flow rates and temperatures.

   (2) Formaldehyde and methanol concentration in top tray (s) liquid.

   (3) Temperature and pressure of feed gas.

   (4) Temperature of the absorber vent gas, especially during warm weather operation.

C. A partially clogged or fouled demister can result in excessive liquid entrainment.

D. When absorber vent gas is burned, proper operation of the combustion device is essential if emissions are to be minimized. Two types of problems may be expected to be encountered, (1) flame-outs and (2) excessive smoking. Plants are likely to periodically record some or all of the following operating variables. Data will also be available on design limits.

   (1) Combustion zone temperature.

   (2) Quantity of excess air (too little will cause smoking, too much can result in flame-outs), which might be indicated by measurements on one or all of the following:

      a. Device draft - inches of water.

      b. Temperature of stack gases.

c. Air flow rate.

(3) Composition and flow rate of waste gas to the device.

(4) Quantity and heating value of supplemental fuel.

(5) Composition of stack gases.

E. Periodic visual checks of flare stack opacity may be the only record kept on the operation of this type of device. However, some plants may record the following data for comparison with design limitations.

(1) Feed composition, temperature and flow rate.

(2) Occasional introduction of unusual materials into the flare header.

(3) Plant up-sets causing changes in loading on the flare system or carryover of liquids to the header.

The investigating operative should be cognizant of the fact that seemingly similar plants may have had widely differing design criteria. Thus, the flow, temperature, pressure, composition, etc. characterizing a given stream in on plant cannot necessarily be used as a basis for estimating like data for the comparable stream in another plant. Nor, can data from similar streams in separate plants be used, in themselves, to estimate comparative efficiencies of related control equipment.

XI. Financial Impact

Table FM-12 presents economics for formaldehyde manufacture in a typical 100 MM Lbs./Year plant. This plant employs neither incineration nor scrubbing devices, but relies solely on absorber off-gas recycling techniques and absorber tower temperature manipulation for emission control. Two cases are shown; the first for the current listed Gulf Coast methanol price of 12¢/gal., and the second for the Los Angeles area price of 17¢/gal. As would be expected, this results in an appreciable difference in return on investment. However, even the operation with the more expensive feedstock is quite profitable.

Table FM-13 shows estimated economics for producing formaldehyde in a new most feasible plant. This plant provides for burning absorber vent gas in an appropriately designed incinerator, without heat recovery.

Table FM-13 indicates that total production costs for the new most feasible plant will be slightly higher than the costs for existing plants. The estimated difference is + .04¢/lb. of 37% formaldehyde. Return on investment for the new most feasible plant is lower by 1.9 to 2.2%. The difference in production costs is based on the assumption that the required fuel for the incinerator will be available at a price of 40¢/MM BTU. Should the cost be higher, then manufacturing costs for the new most feasible plant will be increased proportionately.

No other case has been considered for financial impact studies because:

(1) The cost of installing and operating an incinerator on an existing plant will be about the same as on a new plant.

(2) The addition of heat recovery equipment is not considered to be economically justified.

(3) Flare systems, while costing less to install are more expensive to operate and wasteful of fuel.

(4) Scrubbers, while less expensive to operate, do not achieve as effective a clean-up of air emissions and are more expensive to install, especially on existing plants. Furthermore, they transfer the emission problem to the liquid effluents from the plant.

Obviously, the reader may take exception to any of these positions. In that case, the data of Table FM-11 may be used to study the financial impact of the alternatives.

Table FM-14 presents a proforma balance sheet for the following cases:

(1) An existing plant - with no scrubbing, incineration or fractionator recycle.

(2) Most feasible new - this plant burns absorber tail gas in an incinerator.

It was assumed in developing these asset and liability positions that the formaldehyde selling price would be held constant and the small increase in total production costs would be taken out of the profit margin in order to maintain sales at the same level. Capital requirement for the most feasible new plant is estimated to be about $54,000 higher than for an existing plant of the same capacity - 100 MM lbs./year.

TABLE FM-12
FORMALDEHYDE MANUFACTURING COSTS
FOR A TYPICAL
EXISTING 100 MM LB./YR. FACILITY

	¢/LB.	$/YR.	¢/LB.	$/YR.
DIRECT MANUFACTURING COST				
Raw Materials				
Methanol @ 17¢/Gal.	1.072			
Methanol @ 12¢/Gal.			.757	
Catalysts & Chemicals	.111		.111	
Labor (2 men/shift @ $4.85/Hr.)	.079		.079	
Maintenance (5% of Investment)	.085		.085	
Utilities	.146		.146	
	1.493		1,178	
INDIRECT MANUFACTURING COST				
Plant Overhead (110% of Labor)	.087		.087	
FIXED MANUFACTURING COSTS				
Depreciation (10 years)	.170		.170	
Ins. & Prop. Taxes (2.3% of Inv.)	.039		.039	
	.209		.209	
MANUFACTURING COST	1.789		1.474	
GENERAL EXPENSES				
Administration (3% of mfr. cost)	.054		.044	
Sales (1% of mfr. cost)	.018		.015	
Research (2% of mfr. cost)	.036		.029	
Finance (6% of inv.)	.102		.102	
	.210		.190	
COST				
ex Works	1.999		1.664	
Delivery	.620		.620	
TOTAL DELIVERED COST	2.619	2,619,000	2.284	2,284,000
PRODUCT VALUE				
37% HCHO - Uninhibited @ 3.5¢/lb. (DLVD)	3.500	3,500,000	3.500	3,500,000
Profit before taxes	.881	881,000	1.216	1,216,000
Profit after 52% tax	.423	423,000	.584	584,000
Cash Flow		593,000		754,000
RETURN ON INVESTMENT		24.9%		34.3%

TABLE FM-13
FORMALDEHYDE MANUFACTURING COSTS
FOR A TYPICAL 100 MM LB./YR. FACILITY
EXISTING OR NEW WITH THERMAL INCINERATOR (NO HEAT RECOVERY)

	¢/LB.	$/YR.	¢/LB.	$/YR.
DIRECT MANUFACTURING COST				
Raw Materials				
Methanol @ 17¢/Gal.	1.072			
Methanol @ 1?¢/Gal.			.757	
Catalysts & Chemicals	.111		.111	
Labor (2 men/shift @ $4.85/Hr.)	.080		.080	
Maintenance (5% of Investment)	.088		.088	
Utilities	.172		.172	
	1.523		1.208	
INDIRECT MANUFACTURING COSTS				
Plant Overhead (110% of Labor)	.088		.088	
FIXED MANUFACTURING COSTS				
Depreciation (10 years)	.175		.175	
Ins. & Prop. Taxes (2.3% of Inv.)	.040		.040	
	.215		.215	
MANUFACTURING COSTS	1.826		1.511	
GENERAL EXPENSE				
Administration (3% of Mfr. Cost)	.055		.045	
Sales (1% of Mfr. Cost)	.018		.015	
Research (2% of Mfr. Cost)	.036		.030	
Finance (6% of Inv.)	.105		.105	
	.214		.195	
COST				
Ex Works	2.040		1.706	
Delivery	.620		.620	
TOTAL DELIVERED COST	2.660	2,660,000	2.326	2,326,000
PRODUCT VALUE				
37% HCHO - Uninhibited @ 3.5¢/Lb. (DLVD)	3.500	3,500,000	3.500	3,500,000
Profit before Taxes	.840	840,000	1.174	1,174,000
Profit after 52% Tax	.403	403,000	.564	564,000
Cash Flow		578,000		739,000
RETURN ON INVESTMENT		23.0%		32.1%
ROI SENSITVITY				
With Double Capital Charges*		21.9%		30.8%
With Double Capital & Operating Cost*		21.1%		30.0%

*Based on Table FM-11.

TABLE FM-14
PROFORMA BALANCE SHEET
100 MM LB./YR. FORMALDEHYDE MANUFACTURING FACILITY

	Existing	New or Existing with Thermal Incinerator (No Heat Recovery)
Current Assets		
Cash (A)	149,100	152,000
Accounts Receivable (B)	291,700	291,700
Inventories (C)	199,900	204,000
Fixed Assets		
Plant	1,700,000	1,754,000
Building	50,000	50,000
Land	25,000	25,000
Total Assets	2,415,700	2,476,900
Current Liabilities (D)	192,300	195,000
Equity and Long Term Debt	2,223,400	2,281,900
Total Capital	2,415,700	2,476,900

(A) Based on one month's manufacturing cost (with methanol @ 17¢/gal.).
(B) Based on one month's sales.
(C) Based on 10 MM lbs. of product valued at total cost (ex works).
(D) Based on one month's total cost (DLVD) less fixed manufacturing and finance costs.

An evaluation of the overall environmental impact of the most feasible method of emission control described in this report is as important as the financial impact. In addition to the desirable effect of reducing atmospheric pollution through the curtailment of hydrocarbon and carbon monoxide emissions, one must consider the cost in terms of energy. If all new mixed oxide catalyst process plants employ vent gas incineration, supplemental fuel in the amount of 3.5×10^{11} BTU/year will be required to properly combust the pollutants. This is equivalent to 350 million standard cubic feet per year of natural gas. An additional 300 million SCF/year will be required for the employment of incinerators on all existing plants. Use of flare systems instead of incinerators will approximately double these natural gas consumptions while heat recovery systems on the incinerators could halve them.

XII. Cost to Industry

In the typical present day plant, as depicated in Table FM-12, very little of the plant investment is directly attributable to the cost of air pollution control.

As noted in Section XI, the proposed most feasible modification of existing formaldehyde plants results in negligible effects on production costs (plus .04¢/lb. - Of 37% formaldehyde). Therefore, the addition of incinerators to existing plants should not pose a significant economic problem to the industry. The total investment required to add this device to all existing mixed oxide catalyst process plants would be on the order of $1,000,000.

In the "most feasible new plant" presented in Table FM-13, additional air pollution control equipment represents about three percent of total plant investment. The resulting total production cost will be an estimated .04¢/lb. higher than for the present day typical unit. Thus, the costs involved should not reduce growth in demand via the requirement for higher formaldehyde prices.

Assuming all new mixed oxide catalyst process plants built between now and 1985 incorporate this type of air pollution control equipment, the total incremental capital cost will be on the order of $1,000,000.

The projected effect of the above expenditures on future air emissions is shown in Table FM-15, wherein:

The first three colums depict 1985 emissions for the situation where no pollution control devices (as defined in Section IV) are employed. However, credit is given to new plants which can minimize emissions by running a recycle operation. The total emission rate is estimated to be 87.6 MM lbs./year.

The other three colums show the estimated 1985 emissions with all plants utilizing that mode termed most feasible modification to new or existing facilities, i.e., incinerators on the absorber vent gas stream. This has the effect of lowering the emissions by 96% to 3.34 MM lbs./year.

TABLE FM-15
ESTIMATED 1985 EMISSIONS
FOR
ALTERNATIVE CONTROL SYSTEM

Type of Emission Control	None			Incinerators (1)		
Plants Involved	Existing (2)	New (3)	Total	Existing	New	Total
Production (MM Lbs./Year)	1,729	1,791	3,520	1,729	1,791	3,520
Emissions (Lbs./Lb.)						
Hydrocarbons	0.0149	0.0036	0.0092	0.0014	0.0005	0.00095
Carbon Monoxide	0.0144	0.0170	0.0158	0	0	0
Total	0.0293	0.0206	0.0250	0.0014	0.0005	0.00095
Emissions (MM Lbs./Year)						
Hydrocarbons	25.7	6.5	32.2	2.44	0.90	3.34
Carbon Monoxide	24.9	30.5	55.4	0	0	0
Total	50.6	37.0	87.6	2.44	0.90	3.34
Weighted Emissions (4)						
Hydrocarbons			2560			267
Carbon Monoxide			55			0
Total			2615			267

NOTES:

(1) On absorber vent gas.
(2) Average reported by questionnaire respondents (see Page FM-22).
(3) Utilizing best recycle system (see Page FM-8). Note that this disagrees with data reported on page 2 and 3 of Table I of Appendix I because data on improved recycle operations came to light after Table I was first published.
(4) Weighting Factors: Hydrocarbons = 80, Carbon Monoxide = 1 (see Appendix for explanation).

XIII. Emission Control Deficiencies

The control of formaldehyde plant emissions is effected by the following technical considerations:

A. Process Chemistry and Kinetics

Production of formaldehyde by the mixed oxide catalyst process is based on the air oxidation of methanol. The amount of formaldehyde produced (per unit of methanol) is influenced by a variety of parameters; among which are converter residence time, converter temperature and methanol/oxygen ratio.

1. Converter Feed

(a) Methanol

Methanol feed must be pure. Impurities in the feed will generally end up as impurities in the product. Formic acid, one of the more common formaldehyde contaminants, can be produced through the use of impure methanol. Ion exchange resins are normally used to remove acidic contaminants from the product. Regeneration of these resins may lead to acid waste stream disposal problems.

(b) Air

Air is the source of oxygen required for the primary reaction. Unlike the silver catalyst process, the metal oxide catalyst is not adversely affected by SO_2 and thus the air requires no special treatment prior to its admixture with methanol.

Air is also the source of nitrogen, which constitutes about 75% (for recycle plants) of the absorber vent stream. Because the major portion of the hydrocarbon emissions relating to the subject process are those transported to the atmosphere by venting non-reactants and reaction by-products, then reducing the amount of nitrogen vented should reduce the amount of hydrocarbons emitted. One way this can be done (when using air as the source of oxygen) is to reduce the amount of air charged to the process. This has been accomplished by proceeding from non-recycle type operation to recycle operation. Thus, emission reduction by this technique is probably as far advanced - in modern 'recycle plants' - as practicable.

2. Converter Operating Conditions

Converter operating conditions influence methanol conversion rate and to some extent, the amount of non-selective products formed. One of the non-selective products, (carbon monoxide) is a major component of the absorber vent gas stream. Converter operating conditions are normally selected to obtain the optimum balance between conversion and selectivity.

3. Catalyst

Since there is more than one licensor for the subject process, it seems reasonable to surmise that there are various

catalyst formulations employed by the industry. Unfortunately, detailed comparisons of the available catalysts are not available. As discussed elsewhere in this report, a catalyst that produced no dimethyl ether would be highly desirable from an emission control standpoint.

Catalyst life is stated [4], by one licensee, to be in the range of 18-24 months. It is expected, however, that the increased severity of recycle type operations will result in somewhat shorter life.

B. Process Equipment

1. Absorber

The absorber tail gas contains both gases and uncondensed vapors, The uncondensed hydrocarbon vapors (methanol and formaldehyde), because of their high 'weighted' value constitute the single most significant source of emitted pollutants in the formaldehyde plant. More complete condensation of the hydrocarbons is possible if the absorber pressure is increased or the top temperature is decreased. Unfortunately, neither action is practical. Increasing pressure to a level sufficiently high to significantly affect vapor-liquid equilibria would result in prohibitively high equipment and utility costs. Decreasing the tower top temperature appreciably is impractical because the freezing point of the liquid on the top tray is close to 32° F, which, after allowing for a normal margin of safety, is not significantly lower than the temperature at which many producers actually operate their absorbers.

C. Control Equipment and Operations

The current practice of recycling absorber vent gases provides reasonably good control of hydrocarbon emissions. The emissions can be further reduced by either water scrubbing or incineration. Each method has its own deficiency. Water scrubbing requires relatively high capital investment and is only moderately efficient. Additionally, secondary water treatment is required, although this might only be incremental to the overall plant water treatment costs and thus relatively inexpensive. Incineration, due to high supplemental fuel requirements, is burdened with high operating costs, but is quite efficient.

XIV. Research and Development Goals

If the technological deficiencies discussed in Section XIII are to be overcome, additional R & D is indicated in the following areas:

A. Existing Plants - Improved Catalyst

It would be desirable to have a more selective catalyst in order to produce fewer by-products; particularly by-product hydrocarbons, which are especially objectionable when emitted to the atmosphere. Private communications with the industry indicate that such changes in catalyst performance are feasible and perhaps imminent. Thus, R & D in this area may possibly be already under way. Intensification of existing R & D programs (if any) should be considered.

B. New Plants - Utilization of Pure Oxygen

In addition to the above mentioned R & D area, which has application to both new and existing plants, technology involving the substitution of oxygen for air would require modification of existing facilities or most probably would be applicable only to new plants. The use of oxygen is presumably only feasible in plants utilizing gas recycle. In those plants the oxygen could be diluted to below 10.9 vol. % by mixture with the recycle gas. The effect of high carbon monoxide content recycle gas on conversion, yield, temperature control, etc., will require definition via appropriate R & D programs.

XV. Research and Development Programs

The following proposed projects relate to those areas of R & D which seem to offer the best chance of obtaining a method of reducing emissions from formaldehyde plants.

A. Project A

1. Title - Catalyst Modification Program

2. Objective - To investigate variations in the composition of existing commercial mixed oxide catalysts from the standpoint of the effect of these variations on activity, selectivity, aging characteristics and reduction of by-product formation, especially dimethyl ether,

3. Estimated Project Costs (see Table FM-16 for cost breakdown)

Capital Expenditures	$ 22,100
Operating Costs	
Unit Operations	57,300
Services	22,400
Miscellaneous	4,000
Contingency	52,900
	$158,700

4. Scope - This project would seek to reduce formaldehyde plant emissions by catalyst modification.

5. Program - A catalyst screening unit will be constructed with facilities for the evaluation of the effluent by chromatographic procedures with emphasis on the quantitative analysis of by-products. The normal operating characteristics of the screening unit will be determined by employing a commercial mixed oxide catalyst (Reichhold, Lummus, etc.). Experimental catalysts containing metal oxides (chromium, manganese, copper etc.) as additives to the normal iron-moly oxide catalyst will be screened to determine if by-product formation can be reduced without adversely altering the main catalytic function. Adjustment of physical properties of the catalysts (e.g., pore volume distribution, surface PH, total surface area, etc.) will also be studied.

6. Timetable - It is estimated that the above program will require a total of 12 months to complete.

B. Project B

1. Title - Process Modification Program

2. Objective - To investigate variations or modifications to the existing formaldehyde manufacturing process that would reduce vent gas emissions. Emphasis will be given to the substitution of oxygen for air in the feed.

3. Estimated Project Costs (see Table FM-16 for cost breakdown)

Capital Expenditures	$ 67,100
Operating Costs	
Unit Operations	62,500
Services	11,400
Process Engineering	9,100
Miscellaneous	5,800
Contingency	78,000
Total	$233,900

4. Scope - This program would seek to reduce formaldehyde plant emissions by process modifications.

5. Program

(a) Construction of Pilot Unit

The first phase in this program would be the construction of a small pilot unit. This unit would include converters, quench system, absorber and vent gas recycle facilities and would fully simulate commercial operations. Effluent gases from the converter and absorber will be connected to an on-line gas chromatograph. (If project A and project B are run sequentially, some portions of the project A screening unit might be utilized in the construction of the subject pilot unit.)

(b) A number of process modifications will be explored to determine their effect on methanol conversion, selectivity to formaldehyde and vent gas emissions. The primary thrust of the program, however, will be directed toward evaluating the effect of substituting oxygen for (make-up) air in the feed. In the beginning a standard commercial (or project A variation) mixed oxide catalyst will be used. However, the program will recognize the possibility that catalyst modifications may be necessary to accomodate these changes.

(c) Process Engineering

Date from the process research will be used to develop a model for methanol conversion to formaldehyde. This model will define optimum conversions and selectivities as a function of vent gas emissions.

6. Timetable - It is estimated that the above program will require 17 months to complete.

TABLE FM-16
DETAILED COSTS
FOR
R & D PROJECTS

	Project "A"	Project "L"
A. Capital Expenditures		
Test Unit Construction	$15,000	$60,000
Unit Checkout		
Professional	4,500 (5 weeks)	4,500 (5 weeks)
Operator	2,600 (5 weeks)	2,600 (5 weeks)
B. Operating Expenses		
Unit Operation		
Professional	36,500 (40 weeks)	36,500 (40 weeks)
Operator	20,800 (40 weeks)	26,000 (50 weeks)
Services		
Analytical	1,300 (2 weeks)	3,200 (5 weeks)
Cat. Prep. & Testing	17,500 (35 weeks)	500 (1 week)
Computer Operator		3,200 (6 weeks)
Unit Maint.	3,600 (8 weeks)	4,500 (10 weeks)
C. Process Engineering		
Professional		9,100 (10 weeks)
D. Miscellaneous		
Computer time		2,000
Materials	2,700	2,000
Report Writing	1,300	1,800
E. Totals of A to D	105,800	155,900
Contingency	52,900	78,000
Total Cost	$158,700	$233,900

XVI. Summary of Analytical Methods for Formaldehyde Plant Emissions

Of the seven plants responding to the mixed oxide catalyst formaldehyde process questionnaire, three had measured emissions from the absorber vent stack at some time in the past. The information received as to sampling and analytical techniques was very sketchy, but is summarized below.

One plant has determined formaldehyde and dimethyl ether in the stack gases using a grab sampling technique in conjunction with gas chromatographic analysis. Samples have also been analyzed using the sodium sulfite (1) method. No details regarding gas flow measurements, sampling equipment or chromatograph operation are available. A second plant used a train consisting of absorber vacuum pump and wet test meter followed by analysis of the absorber contents by the sodium sulfite method (1). Gas flow was not measured.

The third plant has sampled for formaldehyde, methanol, dimethyl ether and carbon monoxide. Formaldehyde and dimethyl ether samples were collected in a train consisting of a knockout flask, two Greenberg-Smith impingers containing 250 ml. water each, a rotameter and a vacuum pump. A Fuchsin-sulfurous acid test solution was used for the colorimetric analysis of formaldehyde, while methanol was measured by injection into an F and M Model 720 chromatograph using a 20 foot column packed with ethofat. Dimethyl ether and carbon monoxide samples were collected in a 500 ml. glass bulb preceded by a knockout flask. A vacuum pump was connected to the glass bulb to insure adequate purging. Both dimethyl ether and carbon monoxide were analyzed using a Beckman Model GC-2A gas chromatograph. A 20 foot molecular sieve was used for carbon monoxide, while a column containing 10% triethyl acetyl citrate was used for dimethyl ether. Stack gas flow was monitored during sampling by a flow meter permanently installed in the plant.

The information summarized above is not sufficiently complete to allow a detailed evaluation of the stack sampling techniques used. Considering the information known as to the expected composition of the stack gases, accurate sampling and analysis by glass bulb-gas chromatographic techniques should be readily available. No developmental work appears warranted by the EPA unless a standard method is desired.

A tabular summary of the reported analytical techniques is presented in Table FM-17.

TABLE FM-17
SUMMARY OF
SAMPLING AND ANALYTICAL METHODS

Plant	Component	Method	Make	Model	Column Length - Ft.	Column Packing/Absorbent
14-2	All	Design values used				
14-16	HCHO	Sodium sulfite (Walker)				
	All others	Chromatograph	Microtek	DSS/161	18	10% ethofat, columnpak T
14-17	All	No analytical data offered				
14-19	CH_3OH	Chromatograph	F & M	720	20	Ethofat
	CO	Chromatograph	Beckman	GC-2A	20	Mole sieve
	Dimethyl ether	Chromatograph	Beckman	GC-2A		10% triethyl acetyl citrate
	HCHO	Colorimetric				
14-21	All	Ex pilot plant or design data				
14-22	HCHO	Sodium sulfite (Walker)				
	All others	Design values used				
14-23	All	Ex pilot plant or design data				

FM-46

XVII. Emergency Action Plan For Air Pollution Episodes

A. Types of Episodes

The alleviation of Air Pollution Episodes as suggested by the U.S. Environmental Protection Agency is based on a pre-planned episode emission reduction scheme. The criteria that set this scheme into motion are:

1. Alert Status - The alert level is that concentration of pollutants at which short-term health effects can be expected to occur.

2. Warning Status - The warning level indicates that air quality is continuing to deteriorate and that additional abatement actions are necessary.

3. Emergency Status - The emergency level is that level at which a substantial endangerment to human health can be expected. These criteria are absolute in the sense that they represent a level of pollution that must not be allowed to occur.

B. Sources of Emissions

As outlined in the foregoing in-depth study of formaldehyde manufacture by the Mixed Oxide Catalyst process there are three continuous and two intermittent vent streams to the atmosphere.

1. Continuous Streams

   (a) Absorber Vent - This stream constitutes the greatest potential for air pollution. It consists of the gross converter effluent after cooling and absorption of the product formaldehyde. On most plants surveyed this stream exhausts directly to the atmosphere. The few exceptions use mist eliminators in the tops of the absorber with at least one plant employing a major emission control system in the form of a water scrubber.

   (b) Dowtherm System Vent - This stream is relatively insignificant in its contribution to air pollution. A direct venting to the atmosphere would suggest a "breathing" type of emission. It is, however, reported as a continuous flow that could result from pressure control equipment such as a vacuum ejector.

   (c) Storage Tank Vents - The majority of storage tanks associated with reporting formaldehyde facilities vent directly to the atmosphere. In some cases vapor conservation devices are employed.

2. Intermittent Air Emissions

(a) Catalyst Activation Vent - This stream is the result of a catalyst reactivation procedure whereby relatively large quantities of nitrogen, oxygen and carbon dioxide are vented to the atmosphere for about 24 hours once per year. The stream probably contains trace amounts of ammonium chloride and catalyst dust. However, due to the infrequency of the operation and the low concentration of contaminants, pollution from this source would appear to be negligible.

(b) Compressor Exhaust - Only one respondent reported emissions from this source. Although its purpose is not clear, its composition (N_2, O_2, CO and water) would indicate that it may be from the discharge of the air compressor. Since the reporting plant is a recycling operation, with the recycle stream routed to the suction of the air compressor, the composition would resemble the absorber vent stream. Further, it is stated that during upset conditions which may last for 20-30 minutes, contaminants may leave this source. This would imply that the direct source could be from an "anti-pumping" device on the compressor discharge.

3. Fugitive Emissions

As in any processing plant there are emissions that result from leaks and safing or purging of equipment in preparation for maintenance and spills during loading of rail or truck tankers. These types of emission should be small, infrequent in nature, and, with good housekeeping, negligible as an air pollution source.

C. Abatement Techniques

As the various levels of the pre-planned episode reduction scheme are declared (Alert, Warning and Emergency) a progressive reduction in the amount of air pollutants emitted must be made. This could ultimately lead to total curtailment of pollutant emissions if the emergency level becomes imminent.

The extent of required cutback in emissions from formaldehyde plants will depend on the relative amounts of air pollutants contributed by formaldehyde production to the overall emissions which resulted in the pollution episode. This, plus other factors, will be used by the Governing Environmental Protection Authority in determining the cutback to be made in all air pollution sources during the various episodes.

Formaldehyde manufacturing facilities, via the mixed oxide catalyst process, consist of plants containing a converter, where the reaction takes place, in a multiplicity of tubes filled with catalyst and an absorber with its associated appendages. In most instances formaldehyde manufacturing facilities by the mixed oxide route utilize a recycle of

the absorber overhead. This results in a lower emission rate than would otherwise be possible. It also provides for increased flexibility to effect a partial reduction in air pollutant emissions during an air pollution alert. There are significant differences in design of the various plants. In general, however, on those plants employing a recycle mode of operation, a reduction in emissions can be realized by an increase in the percentage of recycle. This can best be accomplished by decreasing the throughput and increasing the percentage of effluent gas recycle which will result in a reduction in emissions. For those plants that do not conduct a recycle type of operation a partial reduction in emissions can be obtained by an appropriate turndown in production.

It should be noted that the oxidation of methanol is an exothermic reaction with the exotherm consumed within the process to generate steam. Consequently, a significant turndown of plant production could result in a steam deficient condition in the confines of the plant.

Reduction in operating rates result in reductions in emissions from the absorber tail gas. Limited information indicates that emissions decrease at a rate that is more than a linear proportion at lower operating levels. Under normal operation conditions a turndown to a predetermined rate can be accomplished within a twenty-four hour period. There would, however, be a progressive decrease during this period. A shutdown of a methanol converter and its associated equipment in terms of air emissions could be immediate. Startup, however, would depend on conditions maintained during the shutdown. If reaction temperature conditions were maintained through use of the startup heater,then resumption of operation could be immediate. If the unit was allowed to cool to ambient temperature,then startup would require ten to twelve hours.

With one exception,no major emission control devices are reported by the respondents. The exception (14-19) being a water scrubber in use for both the absorber vent gas and storage tank vents prior to discharge to the atmosphere. In plants employing this type of pollution control equipment,it is desirable to maintain design water circulation rates in the scrubber during air pollution episodes. With a reduction in total flow of the absorber vent gas, the scrubbing efficiency should be improved over that obtained at normal formaldehyde production levels.

1. Declaration of Alert Condition - When an alert condition is declared,the episode emission reduction plan is immediately set into motion. Under this plan, in addition to notifying the manufacturers of the alert condition, it may be deemed necessary by the Environmental Protection Authorities to somewhat reduce emissions from formaldehyde manufacture in order to prevent further increases in pollution level which could result in warning or emergency episodes. This reduction would be accomplished by a turndown in plant production as previously discussed. The time required to effect the reduction

will be approximately as stated in the preceding discussion. This will reduce the principal source of emission, represented by the absorber vent stream. The other continuous sources of emissions represented by the dowtherm system and storage tank vents are relatively insignificant in their contribution to air pollution. It would be expected that storage tank vent losses would be reduced to some lesser degree by virtue of the reduction made in the producing equipment.

The intermittent emissions represented by the catalyst activation vent and the compressor exhaust should be curtailed if possible during an air pollution episode. In the case of the compressor exhaust it is indicated that this stream is emitted during upset conditions. With a reduction in the producing equipment it is unlikely that this source of emission would become activated. In any event every effort should be made to prevent a discharge from this source. Usually the alert condition can be expected to continue for twelve hours or more.

2. Declaration of Warning Condition - When the air pollution warning episode is announced a substantial reduction of air contaminants is desirable even to the point of assuming reasonable economic hardship in the cutback of production and allied operations. This could involve a 50-60% decrease in formaldehyde production.

3. Emergency Condition - When it appears that an air pollution episode is imminent, all air contaminants may have to be eliminated immediately by ceasing production and allied operations to the extent possible without causing injury to persons or damage to equipment.

D. Economic Considerations

The economic impact on formaldehyde manufacturers of curtailing operations during any of the air pollution episodes is based on the duration and number of episodes in a given period. It is indicated that the usual duration of air pollution episodes is one to seven days with meteorology episode potentials as high as 80 per year.[19] The frequency of air pollution episodes in any given area is indicated as being one to four per year. These data do not differentiate between the episode levels set forth in the early paragraphs of this section. Normally since the alert level does not require a cutback in production, it will not influence plant economics. Therefore in discussing economic considerations resulting from the air pollution abatement plan, it is only necessary to estimate the frequency and number of warning and emergency episodes. For the economic study, it has been assumed that three warning and no emergency episodes occur per year. Each warning episode is assumed to require a 50% reduction in air contaminants for a period of 5-1/2 days. This equates to a complete loss in plant production of about eight and one-half days per year.

The Financial impact resulting from this loss in production is shown in Table FM-18 which presents comparative manufacturing costs for a typical existing 100 MM lbs./year facility without extensive pollution control (Table FM-12) and a typical existing or new plant of the same capacity but having an absorber vent gas incinerator (Table FM-13). Economics are shown for each of these plants with methanol feed at 12 and 17 cents per gallon with and without the financial impact accredited to the air pollution episodes. It should be noted that whereas the proposed cutback in formaldehyde production for emission control appears small (2.5 percent on a yearly basis), it reduced net profit by 4.0 to 4.5 percent.

E. Summary of Estimated Emissions

In the foregoing a reduction in air pollutant emissions was suggested for the various air pollution levels that may be encountered. This was primarily predicated on existing plants with no pollution control equipment. However, special considerations should be provided in the EPA for Air Pollution Episode Avoidance for existing plants that install control devices which substantially reduce emissions and also for future plants that are equipped with the "latest state of the art" emission control equipment.

The following presents estimated air emissions for typical present-day systems without control devices and a typical existing or new plant that incorporates thermal incineration on the absorber vent gas.

Pollutant	Typical Present-Day System Without Control Devices	Typical New or Existing Plant With Thermal Incineration (No Heat Recovery)
Emissions, Lb./Lb.		
Hydrocarbons	0.0092	.0005
Carbon Monoxide	0.0158	--
Total	0.0250	.0005

As noted in the above, total emissions for the plant with an incinerator have been reduced to two percent of that estimated for the uncontrolled plant. However, for both the new and modified plants with incineration, some NOx emission would be expected.

The particular type and concentration of pollutants in the atmosphere at the time of the episode would dictate the degree to which a reduction would be made. If NOx is the offending material, then a reduction in production from plants with incinerators may be required as outlined under "Declaration of Alert Condition". In this case NOx would be reduced as the cutback in production is made.

If the offending pollutants are in the form of hydrocarbons or carbon monoxide, the degree of cutback on the typical new plant or the modified existing plant could be proportionally less severe than on the uncontrolled facility.

TABLE FM-18

FINANCIAL IMPACT OF AIR POLLUTION EPISODES

ON MANUFACTURING COSTS

FOR 100 MM LBS/YEAR FORMALDEHYDE MANUFACTURING FACILITIES

VIA THE MIXED OXIDE CATALYST PROCESS

	TYPICAL EXISTING PLANT (FROM TABLE FM-12)				TYPICAL NEW PLANT UTILIZING THERMAL INCINERATOR (NO HEAT RECOVERY) (FROM TABLE FM-13)			
	Methanol @ 17¢/Gal.		Methanol @ 12¢/Gal.		Methanol @ 17¢/Gal.		Methanol @ 12¢/Gal.	
	No Cutback In Production	Assuming 8.5 Days Lost Production	No Cutback In Production	Assuming 8.5 Days Lost Production	No Cutback In Production	Assuming 8.5 Days Lost Production	No Cutback In Production	Assuming 8.5 Days Lost Production
Direct Manufacturing Costs, M $/Yr.								
Raw Materials								
Methanol @ 17¢/Gal.	1,072	1,045			1,072	1,045		
Methanol @ 12¢/Gal.			757	738			757	738
Catalyst & Chemicals	111	108	111	108	111	108	111	108
Labor	79	79	79	79	80	80	80	80
Maintenance	85	85	85	85	88	88	88	88
Utilities*	146	142	146	142	172	168	172	168
Indirect Manufacturing Costs, M $/Yr.								
Plant Overhead	87	87	87	87	88	88	88	88
Fixed Manufacturing Costs, M $/Yr.								
Depreciation, Insurance, and Property Taxes	209	209	209	209	215	215	215	215
Manufacturing Costs, M $/Yr.	1,789	1,755	1,474	1,448	1,826	1,792	1,511	1,485

*One formaldehyde manufacturer has commented that these costs are high relative to utility costs on the silver catalyst process.

TABLE FM-18

FINANCIAL IMPACT OF AIR POLLUTION EPISODES

ON MANUFACTURING COSTS

FOR 100 MM LBS/YEAR FORMALDEHYDE MANUFACTURING FACILITIES

VIA THE MIXED OXIDE CATALYST PROCESS

PAGE 2 - CONTINUED

	TYPICAL EXISTING PLANT (FROM TABLE FM-12)				TYPICAL NEW PLANT UTILIZING THERMAL INCINERATOR (NO HEAT RECOVERY) (FROM TABLE FM-13)			
	Methanol @ 17¢/Gal.		Methanol @ 12¢/Gal.		Methanol @ 17¢/Gal.		Methanol @ 12¢/Gal.	
	No Cutback In Production	Assuming 8.5 Days Lost Production	No Cutback In Production	Assuming 8.5 Days Lost Production	No Cutback In Production	Assuming 8.5 Days Lost Production	No Cutback In Production	Assuming 8.5 Days Lost Production
General Expenses								
Administration, Sales, Res., and Finance	210	210	190	190	214	214	195	195
Cost								
Ex Works	1,999	1,965	1,664	1,638	2,040	2,006	1,706	1,680
Delivery	620	605	620	605	620	605	620	605
Total Delivered Costs	2,619	2,570	2,284	2,243	2,660	2,611	2,326	2,285
Product Value, M $/Yr.								
37% HCHO - Uninhibited @ 3.5¢/Lb. (Dlvd.)	3,500	3,413	3,500	3,413	3,500	3,413	3,500	3,413
Profit Before Taxes	881	843	1,216	1,170	840	802	1,174	1,128
Profit After 52% Tax	423	405	584	562	403	385	564	541
Cash Flow	593	575	754	732	578	560	739	716
ROI	24.9%	23.8%	34.3%	33.1%	23.0%	21.9%	32.1%	30.8%

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APPENDIX I-1.

BASIS OF THE STUDY

I. Industry Survey

The study which led to this document was undertaken to obtain information about selected production processes that are practiced in the Petrochemical Industry. The objective of the study was to provide data for the EPA to use in the fulfillment of their obligations under the Clean Air Amendments of 1970.

The information obtained during the study includes industry descriptions, air emission control problems, sources of air emissions, statistics on quantities and types of emissions and descriptions of emission control devices currently in use. The principal source for these data was an Industry Questionnaire but it was supplemented by plant visits, literature searches, in-house background knowledge and direct support from the Manufacturing Chemists Association.

More than 200 petrochemicals are currently produced in the United States, and many of these by two or more different processes. It was obvious that the most immediate need was to study the largest tonnage, fastest growth processes that produce the most pollution. Consequently, the following 32 chemicals (as produced by a total of 41 different processes) were selected for study:

Acetaldehyde (two processes)
Acetic Acid (three processes)
Acetic Anhydride
Acrylonitrile
Adipic Acid
Adiponitrile (two processes)
Carbon Black
Carbon Disulfide
Cyclohexanone
Ethylene
Ethylene Dichloride (two processes)
Ethylene Oxide (two processes)
Formaldehyde (two processes)
Glycerol
Hydrogen Cyanide
Maleic Anhydride
Nylon 6
Nylon 6,6
"Oxo" Alcohols and Aldehydes
Phenol
Phthalic Anhydride (two processes)
Polyethylene (high density)
Polyethylene (low density)
Polypropylene
Polystyrene
Polyvinyl Chloride
Styrene
Styrene - Butadiene Rubber
Terephthalic Acid (1)
Toluene Di-isocyanate (2)
Vinyl Acetate (two processes)
Vinyl Chloride

(1) Includes dimethyl terephthalate.
(2) Includes methylenediphenyl and polymethylene polyphenyl isocyanates.

The Industry Questionnaire, which was used as the main source of information, was the result of cooperative efforts between the EPA, Air Products and the EPA's Industry Advisory Committee. After receiving approval from the Office of Management and Budget, the questionnaire was sent to selected producers of most of the chemicals listed above. The data obtained from the returned questionnaires formed the basis for what have been named "Survey Reports". These have been separately published in four volumes, numbered EPA-450/3-73-005a, b, c, and d and entitled "Survey Reports on Atmospheric Emissions from the Petrochemical Industry - Volumes I, II, III, and IV.

The purpose of the survey reports was to screen the various petrochemical processes into the "more" and "less - significantly polluting processes". Obviously, significance of pollution is a term which is difficult if not impossible to define because value judgements are involved. Recognizing this difficulty, a quantitative method for Significant Emission Index (SEI) was developed. This procedure is discussed and illustrated in Appendix II of this report. Each survey report includes the calculation of an SEI for the petrochemical that is the subject of the report. These SEI's have been incorporated into the Emission Summary Table that constitutes part of this Appendix (Table I). This table can be used as an aid when establishing priorities in the work required to set standards for emission controls on new stationary sources of air pollution in accordance with the terms of the Clean Air Amendments of 1970.

The completed survey reports constitute a preliminary data bank on each of the processes studied. In addition to the SEI calculation, each report includes a general introductory discussion of the process, a process description (including chemical reactions), a simplified process flow diagram, as well as heat and material balances. More pertinent to the air pollution study, each report lists and discusses the sources of air emissions (including odors and fugitive emissions) and the types of air pollution control equipment employed. In tabular form, each reports summarizes the emission data (amount, composition, temperature, and frequency); the sampling and analytical techniques; stack numbers and dimensions; and emission control device data (types, sizes, capital and operating costs, and efficiencies).

Calculation of efficiency on a pollution control device is not necessarily a simple and straight-forward procedure. Consequently, two rating techniques were developed for each type of device, as follows:

1. For flares, incinerators, and boilers a Completeness of Combustion Rating (CCR) and Significance of Emission Reduction Rating (SERR) were used.

2. For scrubbers and dust removal equipment, a Specific Pollutant Efficiency (SE) and a SERR were used.

The bases for these ratings and example calculations are included in Appendix III of this report.

II. In-Depth Studies

The original performance concept was to select a number of petrochemical processes as "significant polluters", on the basis of data contained in completed questionnaires. These processes were then to be studied "in-depth". However, the overall time schedule was such that the EPA requested an initial selection of three processes on the basis that they would probably turn out to be "significant polluters". The processes selected in this manner were:

1. The Furnace Process for producing Carbon Black.

2. The Sohio Process for producing Acrylonitrile.

3. The Oxychlorination Process for producing 1,2 Dichloroethane (Ethylene Dichloride) from Ethylene.

TABLE I
EMISSIONS SUMMARY

	ESTIMATED (1) CURRENT AIR EMISSIONS, MM LBS./YEAR						
	Hydrocarbons (3)	Particulates (4)	Oxides of Nitrogen	Sulfur Oxides	Carbon Monoxide	Total	Total Weighted (5)
Acetaldehyde via Ethylene	1.1	0	0	0	0	1.1	86
via Ethanol	0	0	0	0	27	27	27
Acetic Acid via Methanol	0	0	0.01	0	0	0.01	1
via Butane	40	0	0.04	0	14	54	3,215
via Acetaldehyde	6.1	0	0	0	1.3	7.4	490
Acetic Anhydride via Acetic Acid	3.1	0	0	0	5.5	8.6	253
Acrylonitrile (9)	183	0	5.5	0	196	385	15,000
Adipic Acid	0	0.2	29.6	0	0.14	30	1,190
Adiponitrile via Butadiene	11.2	4.7	50.5	0	0	66.4	3,200
via Adipic Acid	0	0.5	0.04	0	0	0.54	30
Carbon Black	156	8.1	6.9	21.6	3,870	4,060	17,544
Carbon Disulfide	0.15	0.3	0.1	4.5	0	5.1	120
Cyclohexanone	70	0	0	0	77.5	148	5,700
Dimethyl Terephthalate (+TPA)	91	1.4	0.1	1.0	53	146.5	7,460
Ethylene	15	0.2	0.2	2.0	0.2	17.6	1,240
Ethylene Dichloride via Oxychlorination	95.1	0.4	0	0	21.8	117.3	7,650
via Direct Chlorination	29	0	0	0	0	29	2,300
Ethylene Oxide	85.8	0	0.3	0.1	0	86.2	6,880
Formaldehyde via Silver Catalyst	23.8	0	0	0	107.2	131	1,955
via Iron Oxide Catalyst	25.7	0	0	0	24.9	50.6	2,070
Glycerol via Epichlorohydrin	16	0	0	0	0	16	1,280
Hydrogen Cyanide Direct Process	0.5	0	0.41	0	0	0.91	56
Isocyanates	1.3	0.8	0	0.02	86	88	231
Maleic Anhydride	34	0	0	0	260	294	2,950
Nylon 6	0	1.5	0	0	0	1.5	90
Nylon 6,6	0	5.5	0	0	0	5.5	330
Oxo Process	5.25	0.01	0.07	0	19.5	24.8	440
Phenol	24.3	0	0	0	0	24.3	1,940
Phthalic Anhydride via O-Xylene	0.1	5.1	0.3	2.6	43.6	51.7	422
via Naphthalene	0	1.9	0	0	45	47	160
High Density Polyethylene	79	2.3	0	0	0	81.3	6,400
Low Density Polyethylene	75	1.4	0	0	0	76.4	6,100
Polypropylene	37.5	0.1	0	0	0	37.6	2,950
Polystyrene	20	0.4	0	1.2	0	21.6	1,650
Polyvinyl Chloride	62	12	0	0	0	74	5,700
Styrene	4.3	0.07	0.14	0	0	4.5	355
Styrene-Butadiene Rubber	9.4	1.6	0	0.9	0	12	870
Vinyl Acetate via Acetylene	5.3	0	0	0	0	5.3	425
via Ethylene	0	0	TR	0	0	TR	TR
Vinyl Chloride	17.6	0.6	0	0	0	18.2	1,460
Totals	1,227.6	49.1	94.2	33.9	4,852.6	6,225.9 (7)	110,220 (7)

(1) In most instances numbers are based on less than 100% survey. All based on engineering judgement of best current control. Probably has up to 10% low bias.
(2) Assumes future plants will employ best current control techniques.
(3) Excludes methane, includes H_2S and all volatile organics.
(4) Includes non-volatile organics and inorganics.
(5) Weighting factors used are: hydrocarbons - 80, particulates - 60, NO_x - 40, SO_x - 20, and CO - 1.
(6) Referred to elsewhere in this study as "Significant Emission Index" or "SEI".
(7) Totals are not equal across and down due to rounding.
(9) Emissions based on what is now an obsolete catalyst. See Report No. EPA-450/3-73-006 b for up-to-date information.

TABLE I
EMISSION SUMMARY

ESTIMATED ADDITIONAL (2) AIR EMISSIONS IN 1980, MM LBS./YEAR

	Hydrocarbons (3)	Particulates (4)	Oxides of Nitrogen	Sulfur Oxides	Carbon Monoxide	Total	Total Weighted (5,6)
Acetaldehyde via Ethylene	1.2	0	0	0	0	1.2	96
via Ethanol	0	0	0	0	0	0	0
Acetic Acid via Methanol	0	0	0.04	0	0	0.04	2
via Butane	0	0	0	0	0	0	0
via Acetaldehyde	12.2	0	0	0	2.5	14.7	980
Acetic Anhydride via Acetic Acid	0.73	0	0	0	1.42	2.15	60
Acrylonitrile (9)	284	0	8.5	0	304	596	23,000
Adipic Acid	0	0.14	19.3	0	0.09	19.5	779
Adiponitrile via Butadiene	10.5	4.4	47.5	0	0	62.4	3,010
via Adipic Acid	0	0.5	0.04	0	0	0.54	30
Carbon Black	96	3.3	2.8	8.9	1,590	1,670	7,200
Carbon Disulfide	0.04	0.07	0.03	1.1	0	1.24	30
Cyclohexanone	77.2	0	0	0	85.1	162	6,260
Dimethyl Terephthalate (+TPA)	73.8	1.1	0.07	0.84	42.9	118.7	4,750
Ethylene	14.8	0.2	0.2	61.5	0.2	77	2,430
Ethylene Dichloride via Oxychlorination	110	0.5	0	0	25	136	8,800
via Direct Chlorination	34.2	0	0	0	0	34.2	2,740
Ethylene Oxide	32.8	0	0.15	0.05	0	33	2,650
Formaldehyde via Silver Catalyst	14.8	0	0	0	66.7	81.5	1,250
via Iron Oxide Catalyst	17.6	0	0	0	17.0	34.6	1,445
Glycerol via Epichlorohydrin	8.9	0	0	0	0	8.9	700
Hydrogen Cyanide Direct Process	0	0	0	0	0	0	0
Isocyanates	1.2	0.7	0	0.02	85	87	225
Maleic Anhydride	31	0	0	0	241	272	2,720
Nylon 6	0	3.2	0	0	0	3.2	194
Nylon 6,6	0	5.3	0	0	0	5.3	318
Oxo Process	3.86	0.01	0.05	0	14.3	18.2	325
Phenol	21.3	0	0	0	0	21.3	1,704
Phthalic Anhydride via O-Xylene	0.3	13.2	0.8	6.8	113	134	1,100
via Naphthalene	0	0	0	0	0	0	0
High Density Polyethylene	210	6.2	0	0	0	216	17,200
Low Density Polyethylene	262	5	0	0	0	267	21,300
Polypropylene	152	0.5	0	0	0	152.5	12,190
Polystyrene	20	0.34	0	1.13	0	21.47	1,640
Polyvinyl Chloride	53	10	0	0	0	63	4,840
Styrene	3.1	0.05	0.1	0	0	3.25	225
Styrene-Butadiene Rubber	1.85	0.31	0	0.18	0	2.34	170
Vinyl Acetate via Acetylene	4.5	0	0	0	0	4.5	360
via Ethylene	0	0	TR	0	0	TR	TR
Vinyl Chloride	26.3	0.9	0	0	0	27.2	2,170
Totals	1,547.2	55.9	79.5	80.5	2,588	4,351.9	134,213 (7)

(1) In most instances numbers are based on less than 100% survey. All based on engineering judgement of best current control. Probably has up to 10% low bias.
(2) Assumes future plants will employ best current control techniques.
(3) Excludes methane, includes H_2S and all volatile organics.
(4) Includes non-volatile organics and inorganics.
(5) Weighting factors used are: hydrocarbons - 80, particulates - 60, NO_x - 40, SO_x - 40, and CO - 1.
(6) Referred to elsewhere in this study as "Significant Emission Index" or "SEI".
(7) Totals are not equal across and down duw to rounding.
(9) See sheet 1 of 3.

TABLE I
EMISSION SUMMARY

ESTIMATED ADDITIONAL (2) AIR EMISSIONS IN 1980, MM LBS./YEAR

	Hydrocarbons (3)	Particulates (4)	Oxides of Nitrogen	Sulfur Oxides	Carbon Monoxide	Total	Total Weighted (5,6)
Acetaldehyde via Ethylene	1.2	0	0	0	0	1.2	96
via Ethanol	0	0	0	0	0	0	0
Acetic Acid via Methanol	0	0	0.04	0	0	0.04	2
via Butane	0	0	0	0	0	0	0
via Acetaldehyde	12.2	0	0	0	2.5	14.7	980
Acetic Anhydride via Acetic Acid	0.73	0	0	0	1.42	2.15	60
Acrylonitrile (9)	284	0	8.5	0	304	596	23,000
Adipic Acid	0	0.14	19.3	0	0.09	19.5	779
Adiponitrile via Butadiene	10.5	4.4	47.5	0	0	62.4	3,010
via Adipic Acid	0	0.5	0.04	0	0	0.54	30
Carbon Black	64	3.3	2.8	8.9	1,590	1,670	7,200
Carbon Disulfide	0.04	0.07	0.03	1.1	0	1.24	30
Cyclohexanone	77.2	0	0	0	85.1	162	6,260
Dimethyl Terephthalate (+TPA)	73.8	1.1	0.07	0.84	42.9	118.7	6,040
Ethylene	14.8	0.2	0.2	61.5	0.2	77	2,430
Ethylene Dichloride via Oxychlorination	110	0.5	0	0	25	136	8,800
via Direct Chlorination	34.2	0	0	0	0	34.2	2,740
Ethylene Oxide	32.8	0	0.15	0.05	0	33	2,650
Formaldehyde via Silver Catalyst	14.8	0	0	0	66.7	81.5	1,250
via Iron Oxide Catalyst	17.6	0	0	0	17.0	34.6	1,445
Glycerol via Epichlorohydrin	8.9	0	0	0	0	8.9	700
Hydrogen Cyanide Direct Process	0	0	0	0	0	0	0
Isocyanates	1.2	0.7	0	0.02	85	87	225
Maleic Anhydride	31	0	0	0	241	272	2,720
Nylon 6	0	3.2	0	0	0	3.2	194
Nylon 6,6	0	5.3	0	0	0	5.3	318
Oxo Process	3.86	0.01	0.05	0	14.3	18.2	325
Phenol	21.3	0	0	0	0	21.3	1,704
Phthalic Anhydride via O-Xylene	0.3	13.2	0.8	6.8	113	134	1,100
via Naphthalene	0	0	0	0	0	0	0
High Density Polyethylene	210	6.2	0	0	0	216	17,200
Low Density Polyethylene	262	5	0	0	0	267	21,300
Polypropylene	152	0.5	0	0	0	152.5	12,190
Polystyrene	20	0.34	0	1.13	0	21.47	1,640
Polyvinyl Chloride	53	10	0	0	0	63	4,840
Styrene	3.1	0.05	0.1	0	0	3.25	225
Styrene-Butadiene Rubber	1.85	0.31	0	0.18	0	2.34	170
Vinyl Acetate via Acetylene	4.5	0	0	0	0	4.5	360
via Ethylene	0	0	TR	0	0	TR	TR
Vinyl Chloride	26.3	0.9	0	0	0	27.2	2,170
Totals	1,547.2	55.9	79.5	80.5	2,588	4,351.9	134,213 (7)

(1) In most instances numbers are based on less than 100% survey. All based on engineering judgement of best current control. Probably has up to 10% low bias.
(2) Assumes future plants will employ best current control techniques.
(3) Excludes methane, includes H_2S and all volatile organics.
(4) Includes non-volatile organics and inorganics.
(5) Weighting factors used are: hydrocarbons - 80, particulates - 60, NO_x - 40, SO_x - 40, and CO - 1.
(6) Referred to elsewhere in this study as "Significant Emission Index" or "SEI".
(7) Totals are not equal across and down due to rounding.
(9) See sheet 1 of 3.

TABLE I
EMISSIONS SUMMARY

	Emissions (2), MM Lbs./Year		Estimated Number of New Plants (1973 - 1980)	Total Estimated Capacity MM Lbs./Year	
	Total by 1980	Total Weighted (5) by 1980		Current	By 1980
Acetaldehyde via Ethylene	2.3	182	6	1,160	2,460
via Ethanol	27	27	0	966	966
Acetic Acid via Methanol	0.05	3	4	400	1,800
via Butane	54	3,215	0	1,020	500
via Acetaldehyde	22	1,470	3	875	2,015
Acetic Anhydride via Acetic Acid	10.8	313	3	1,705	2,100
Acrylonitrile (9)	980	38,000	5	1,165	3,700 (8)
Adipic Acid	50	1,970	7	1,430	2,200
Adiponitrile via Butadiene	128.8	6,210	4	435	845
via Adipic Acid	1.1	60	3	280	550
Carbon Black	5,730	24,740	13	3,000	5,000 (8)
Carbon Disulfide	6.3	150	2	871	1,100
Cyclohexanone	310	11,960	10	1,800	3,600
Dimethyl Terephthalate (+TPA)	265	13,500	8	2,865	5,900
Ethylene	94	3,670	21	22,295	40,000
Ethylene Dichloride via Oxychlorination	253	16,450	8	4,450	8,250 (8)
via Direct Chlorination	63	5,040	10	5,593	11,540
Ethylene Oxide	120	9,530	15	4,191	6,800 (8)
Formaldehyde via Silver Catalyst	212.5	3,205	40	5,914	9,000
via Iron Oxide Catalyst	85	3,515	12	1,729	3,520 (8)
Glycerol via Epichlorohydrin	25	2,000	1	245	380
Hydrogen Cyanide Direct Process	0.5 (10)	28 (10)	0	412	202
Isocyanates	175	456	10	1,088	2,120
Maleic Anhydride	566	5,670	6	359	720
Nylon 6	4.7	284	10	486	1,500
Nylon 6,6	10.8	650	10	1,523	3,000
Oxo Process	43	765	6	1,727	3,000
Phenol	46	3,640	11	2,363	4,200
Phthalic Anhydride via O-Xylene	186	1,522	6	720	1,800 (8)
via Naphthalene	47	160	0	603	528
High Density Polyethylene	297	23,600	31	2,315	8,500
Low Density Polyethylene	343	27,400	41	5,269	21,100
Polypropylene	190	15,140	32	1,160	5,800
Polystyrene	43	3,290	23	3,500	6,700
Polyvinyl Chloride	137	10,540	25	4,375	8,000
Styrene	7.4	610	9	5,953	10,000
Styrene-Butadiene Rubber	14	1,040	4	4,464	5,230
Vinyl Acetate via Acetylene	9.8	785	1	206	356
via Ethylene	TR	TR	4	1,280	2,200
Vinyl Chloride	45	3,630	10	5,400	13,000
Totals	10,605 (7)	244,420 (7)			

(1) In most instances numbers are based on less than 100% survey. All based on engineering judgement of best current control. Probably has up to 10% low bias.
(2) Assumes future plants will employ best current control techniques.
(3) Excludes methane, includes H_2S and all volatile organics.
(4) Includes non-volatile organics and inorganics.
(5) Weighting factors used are: hydrocarbons - 80, particulates - 60, NO_x - 40, SO_x - 20, and CO - 1.
(6) Referred to elsewhere in this study as "Significant Emission Index" or "SEI".
(7) Totals are not equal across and down due to rounding.
(8) By 1985.
(9) See sheet 1 of 3
(10) Due to anticipated future shut down of marginal plants.

In order to obtain data on these processes, the operators and/or licensors of each were approached directly by Air Products' personnel. This, of course, was a slow and tedious method of data collection because mass mailing techniques could not be used, nor could the request for data be identified as an "Official EPA Requirement". Yet, by the time that OMB approval was given for use of the Industry Questionnaire, a substantial volume of data pertaining to each process had already been received. The value of this procedure is indicated by the fact that first drafts of these three reports had already been submitted to the EPA, and reviewed by the Industry Advisory Committee, prior to the completion of many of the survey reports.

In addition, because of timing requirements, the EPA decided that three additional chemicals be "nominated" for in-depth study. These were phthalic anhydride, formaldehyde and ethylene oxide. Consequently, four additional in-depth studies were undertaken, as follows:

1. Air Oxidation of Ortho-Xylene to produce Phthalic Anhydride.

2. Air Oxidation of Methanol in a Methanol Rich Process to produce Formaldehyde over a Silver Catalyst. (Also, the subject of a survey report.)

3. Air Oxidation of Methanol in a Methanol-Lean Process to produce Formaldehyde over an Iron Oxide Catalyst.

4. Direct Oxidation of Ethylene to produce Ethylene Oxide.

The primary data source for these was the Industry Questionnaire, although SEI rankings had not been completed by the time the choices were made.

The Survey Reports, having now been completed are available, for use in the selection of additional processes for in-depth study.

INTRODUCTION TO APPENDIX II AND III

The following discussions describe techniques that were developed for the single purpose of providing a portion of the guidance required in the selection of processes for in-depth study. It is believed that the underlying concepts of these techniques are sound. However, use of them without substantial further refinement is discouraged because the data base for their specifics is not sufficiently accurate for wide application. The subjects covered in the Appendix II discussion are:

1. Prediction of numbers of new plants.

2. Prediction of emissions from the new plants on a weighted (significance) basis.

The subject covered in the Appendix III discussion is:

Calculation of pollution control device efficiency on a variety of bases, including a weighted (significance) basis.

It should be noted that the weighting factors used are arbitrary. Hence, if any reader of this report wishes to determine the effect of different weighing factors, the calculation technique permits changes in these, at the reader's discretion.

APPENDIX II-1.

Number of New Plants*

Attached Table 1 illustrates the format for this calculation. Briefly, the procedure is as follows:

1. For each petrochemical that is to be evaluated, estimate what amount of today's production capacity is likely to be on-stream in 1980. This will be done by subtracting plants having marginal economics due either to their size or to the employment of an out-of-date process.

2. Estimate the 1980 demand for the chemical and assume a 1980 installed capacity that will be required in order to satisfy this demand.

3. Estimate the portion of the excess of the 1980 required capacity over today's remaining capacity that will be made up by installation of each process that is being evaluated.

4. Estimate an economic plant or unit size on the basis of today's technology.

5. Divide the total required new capacity for each process by the economic plant size to obtain the number of new units.

In order to illustrate the procedure, data have been incorporated into Table I, for the three processes for producing carbon black, namely the furnace process, the relatively non-polluting thermal process, and the non-growth channel process.

*The format is based on 1980, but any future year may be selected.

Table 1. Number of New Plants by 1980

Chemical	Process	Current Capacity	Marginal Capacity	Current Capacity on-stream in 1980	Demand 1980	Capacity 1980	Capacity to be Added	Economic Plant Size	Number of New Units
Carbon Black	Furnace	4,000	0	4,000	4,500	5,000	1,000	90	11 - 12
	Channel	100	0	100	100	100	0	30	0
	Thermal	200	0	200	400	500	300	150	2

Notes: 1. Capacity units all in MM lbs./year.

2. 1980 demand based on studies prepared for EPA by Processes Research, Inc. and MSA Research Corporation.

Increased Emissions (Weighted) by 1980

Attached Table 2 illustrates the format for this calculation. However, more important than format is a proposal for a weighting basis. There is a wide divergence of opinion on which pollutants are more noxious and even when agreement can be reached on an order of noxiousness, disagreements remain as to relative magnitudes for tolerance factors. In general pollutants from the petrochemical industry can be broken down into categories of hydrogen sulfide, hydrocarbons, particulates, carbon monoxide, and oxides of sulfur and nitrogen. Of course, two of these can be further broken down; hydrocarbons into paraffins, olefins, chlorinated hydrocarbons, nitrogen or sulfur bearing hydrocarbons, etc. and particulates into ash, catalyst, finely divided end products, etc. It was felt that no useful end is served by creating a large number of sub-groupings because it would merely compound the problem of assigning a weighting factor. Therefore, it was proposed to classify all pollutants into one of five of the six categories with hydrogen sulfide included with hydrocarbons.

There appears to be general agreement among the experts that carbon monoxide is the least noxious of the five and that NO_x is somewhat more noxious than SO_x. However, there are widely divergent opinions concerning hydrocarbons and particulates - probably due to the fact that these are both widely divergent categories. In recent years, at least two authors have attempted to assign tolerance factors to these five categories. Babcock (1), based his on the proposed 1969 California standards for one hour ambient air conditions with his own standard used for hydrocarbons.

On the other hand, Walther (2), based his ranking on both primary and secondary standards for a 24-hour period. Both authors found it necessary to extrapolate some of the basic standards to the chosen time period. Their rankings, on an effect factor basis with carbon monoxide arbitrarily used as a reference are as follows:

	Babcock	Walther	
		Primary	Secondary
Hydrocarbons	2.1	125	125
Particulates	107	21.5	37.3
NO_x	77.9	22.4	22.4
SO_x	28.1	15.3	21.5
CO	1	1	1

Recognizing that it is completely unscientific and potentially subject to substantial criticism it was proposed to take arithmetic averages of the above values and round them to the nearest multiple of ten to establish a rating basis as follows:

	Average	Rounded
Hydrocarbons	84.0	80
Particulates	55.3	60
NO_x	40.9	40
SO_x	21.6	20
CO	1	1

Table 2. Weighted Emission Rates

Chemical _____

Process _____

Increased Capacity _____

Pollutant	Emissions, Lbs./Lb.	Increased Emissions Lbs./Year	Weighting Factors	Weighted Emissions Lbs./Year
Hydrocarbons			80	
Particulates			60	
NO_x			40	
SO_x			20	
CO			1	
			Total	

Increased Emissions (Weighted) by 1980 (continued)

This ranking can be defended qualitatively, if not quantitatively for the following reasons:

1. The level of noxiousness follows the same sequence as is obtained using national air quality standards.

2. Approximately two orders of magnitude exist between top and bottom rankings.

3. Hydrocarbons should probably have a lower value than in the Walther analysis because such relatively non-noxious compounds as ethane and propane are included.

4. Hydrocarbons should probably have a higher value than in the Babcock analysis because such noxious (or posionous) substances as aromatics, chlorinated hydrocarbons, phenol, formaldehyde, and cyanides are included.

5. Particulates should probably have a higher value than in the Walther analysis because national air standards are based mostly on fly ash while emissions from the petrochemical industry are more noxious being such things as carbon black, phthalic anhydride, PVC dust, active catalysts, etc.

6. NO_x should probably have a higher value than in the Walther analysis because its role in oxidant synthesis has been neglected. This is demonstrated in Babcock's analysis.

Briefly, the procedure, using the recommended factors and Table 2, is as follows:

1. Determine the emission rate for each major pollutant category in terms of pounds of pollutant per pound of final product. (This determination was made, on the basis of data reported on returned questionnaires, in the Survey Reports).

2. Multiply these emission rates by the estimate of increased production capacity to be installed by 1980 (as calculated while determining the number of new plants), to determine the estimated pounds of new emissions of each pollutant.

3. Multiply the pounds of new emissions of each pollutant by its weighting factor to determine a weighted pounds of new emissions for each pollutant.

4. Total the weighted pounds of new emissions for all pollutants to obtain an estimate of the significance of emission from the process being evaluated. It was proposed that this total be named "Significant Emission Index" and abbreviated "SEI".

It should be pointed out that the concepts outlined above are not completely original and considerable credit should be given to Mr. L. B. Evans of the EPA for setting up the formats of these evaluating procedures.

Increased Emissions (Weighted) by 1980 (continued)

(1) Babcock, L. F., "A Combined Pollution Index for Measurement of Total Air Pollution," JAPCA, October, 1970; Vol. 20, No. 10; pp 653-659

(2) Walther, E. G., "A Rating of the Major Air Pollutants and Their Sources by Effect", JAPCA, May, 1972; Vol. 22, No. 5; pp 352-355

Appendix III - 1.
Efficiency of Pollution Control Devices

Incinerators and Flares

The burning process is unique among the various techniques for reducing air pollution in that it does not remove the noxious substance but changes it to a different and hopefully less noxious form. It can be, and usually is, a very efficient process when applied to hydrocarbons, because when burned completely the only products of combustion are carbon dioxide and water. However, if the combustion is incomplete a wide range of additional products such as cracked hydrocarbons, soot and carbon monoxide might be formed. The problem is further complicated if the hydrocarbon that is being burned is halogenated, contains sulfur or is mixed with hydrogen sulfide, because hydrogen chloride and/or sulfur oxides then become products of combustion. In addition, if nitrogen is present, either as air or nitrogenated hydrocarbons, oxides of nitrogen might be formed, depending upon flame temperature and residence time.

Consequently, the definition of efficiency of a burner, as a pollution control device, is difficult. The usual definition of percentage removal of the noxious substance in the feed to the device is inappropriate, because with this definition, a "smoky" flare would achieve the same nearly 100 percent rating, as a "smokeless" one because most of the feed hydrocarbon will have either cracked or burned in the flame. On the other hand, any system that rates efficiency by considering only the total quantity of pollutant in both the feed to and the effluent from the device would be meaningless. For example, the complete combustion of one pound of hydrogen sulfide results in the production of nearly two pounds of sulfur dioxide, or the incomplete combustion of one pound of ethane could result in the production of nearly two pounds of carbon monoxide.

For these reasons, it was proposed that two separate efficiency rating be applied to incineration devices. The first of these is a "Completeness of Combustion Rating" and the other is a "Significance of Emission Reduction Rating", as follows:

1. Completeness of Combustion Rating (CCR)

This rating is based on oxygen rather than on pollutants and is the pounds of oxygen that react with the pollutants in the feed to the device, divided by the theoretical maximum number of pounds that would react: Thus a smokeless flare would receive a 100 percent rating while a smoky one would be rated somewhat less, depending upon how incomplete the combustion.

In utilizing this rating, it is clear that carbon dioxide and water are the products of complete combustion of hydrocarbons. However, some question could occur as to the theoretical completion of combustion when burning materials other than hydrocarbons. It was recommended that the formation of HX be considered complete combustion of halogenated hydrocarbons since the oxidation most typically does not change the valence of the halogen. On the other hand, since some incinerators will be catalytic in nature it was recommended that sulfur trioxide be considered as complete oxidation of sulfur bearing compounds.

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Efficiency of Pollution Control Devices

1. Completeness of Combustion Rating (CCR) (continued)

Nitrogen is more complex, because of the equilibria that exist between oxygen, nitrogen, nitric oxide, nitrogen dioxide and the various nitrogen radicals such as nitrile. In fact, many scientists continue to dispute the role of fuel nitrogen versus ambient nitrogen in the production of NO_x. In order to make the CCR a meaningful rating for the incineration of nitrogenous wastes it was recommended that complete combustion be defined as the production of N_2, thus assuming that all NO_x formed comes from the air rather than the fuel, and that no oxygen is consumed by the nitrogen in the waste material. Hence, the CCR becomes a measure of how completely the hydrocarbon content is burned, while any NO_x produced (regardless of its source) will be rated by the SERR as described below.

2. Significance of Emission Reduction Rating (SERR)

This rating is based primarily on the weighting factors that were proposed above. All air pollutants in the feed to the device and all in the effluents from the device are multiplied by the appropriate factor. The total weighted pollutants in and out are then used in the conventional manner of calculating efficiency of pollutant removal, that is pollutants in minus pollutants out, divided by pollutants in, gives the efficiency of removal on a significance of emission basis.

Several examples will serve to illustrate these rating factors. as follows:

Example 1 - One hundred pounds of ethylene per unit time is burned in a flare, in accordance with the following reaction:

$$3C_2H_4 + 7\,O_2 \longrightarrow C + 2\,CO + 3\,CO_2 + 6\,H_2O$$

Thus, 14.2 lbs. of particulate carbon and 66.5 lbs. of carbon monoxide are emitted, and 265 lbs. of oxygen are consumed.

Theoretical complete combustion would consume 342 lbs. of oxygen in accordance with the following reaction:

$$C_2H_4 + 3\,O_2 \longrightarrow 2\,CO_2 + 2\,H_2O$$

Thus, this device would have a CCR of 265/342 or 77.5%

Assuming that one pound of nitric oxide is formed in the reaction as a result of the air used for combustion (this is about equivalent to 100 ppm), a SERR can also be calculated. It should be noted that the formation of this NO is not considered in calculating a CCR because it came from nitrogen in the air rather than nitrogen in the pollutant being incinerated. The calculation follows:

Efficiency of Pollution Control Devices

2. Significance of Emission Reduction Rating (SERR) (continued)

Pollutant	Weighting Factor	Pounds in		Pounds out	
		Actual	Weighted	Actual	Weighted
Hydrocarbons	80	100	8000	0	
Particulates	60	0		14.2	852
NO_x	40	0		1	40
SO_x	20	0		0	
CO	1	0		66.5	66.5
Total			8000		958.5

$$SERR = \frac{8000 - 958.5}{8000} \times 100 = 88\%$$

Example 2 - The same as Example 1, except the hydrocarbons are burned to completion. Then,

$$CCR = \frac{342}{342} \times 100 = 100\%$$

and

$$SERR = \frac{8000 - 40}{8000} = 99.5\%$$

Example 3 - One hundred pounds per unit time of methyl chloride is incinerated, in accordance with the following reaction.

$$2\ CH_3Cl + 3\ O_2 \longrightarrow 2\ CO_2 + 2\ H_2O + 2\ HCl$$

This is complete combustion, by definition, therefore, the CCR is 100%. However, (assuming no oxides of nitrogen are formed), the SERR is less than 100% because 72.5 lbs. of HCl are formed. Hence, considering HCl as an aerosol or particulate;

$$SERR = \frac{100 \times 80 - 72.5 \times 60}{100 \times 80} \times 100 = 45.5\%$$

The conclusion from this final example, of course, is that it is an excellent combustion device but a very poor pollution control device, unless it is followed by an efficient scrubber for HCl removal.

Example 4 - The stacks of two hydrogen cyanide incinerators, each burning 100 pounds per unit time of HCN are sampled. Neither has any carbon monoxide or particulate in the effluent. However, the first is producing one pound of NO_x and the second is producing ten pounds of NO_x in the same unit time. The assumed reactions are:

Efficiency of Pollution Control Devices

2. Significance of Emission Reduction Rating (SERR) (continued)

$$4\ HCN + 5\ O_2 \longrightarrow 2\ H_2O + 4\ CO_2 + 2\ N_2$$

$$N_2\ (\text{atmospheric}) + XO_2 \longrightarrow 2\ NO_x$$

Thus, $CCR_1 = 100\%$ and $CCR_2 = 100\%$ both by definition.

However, $SERR_1 = \frac{100 \times 80 - 1 \times 40}{100 \times 80} \times 100 = 99.5\%$

and $SERR_2 = \frac{100 \times 80 - 10 \times 40}{100 \times 80} \times 100 = 95\%$

Obviously, if either of these were "smoky" then both the CCR and the SERR would be lower, as in Example 1.

Other Pollution Control Devices

Most pollution control devices, such as bag filters, electrostatic precipitators and scrubbers are designed to physically remove one or more noxious substances from the stream being vented. Typically, the efficiency of these devices is rated relative only to the substance which they are designed to remove and for this reason could be misleading. For example:

1. The electrostatic precipitator on a power house stack might be 99% efficient relative to particulates, but will remove little or none of the SO_x and NO_x which are usually present.

2. A bag filter on a carbon black plant will remove 99 + % of the particulate but will remove none of the CO and only relatively small amounts of the compounds of sulfur that are present.

3. A water scrubber on a vinyl chloride monomer plant will remove all of the hydrogen chloride but only relatively small amounts of the chlorinated hydrocarbons present.

4. An organic liquid scrubber on an ethylene dichloride plant will remove nearly all of the EDC but will introduce another pollutant into the air due to its own vapor pressure.

For these reasons, it was suggested again that two efficiency ratings be applied. However, in this case, the first is merely a specific efficiency as is typically reported, i.e., "specific to the pollutant (or pollutants) for which it was designed", thus:

$$SE = \frac{\text{specific pollutant in} - \text{specific pollutant out}}{\text{specific pollutant in}} \times 100$$

The second rating proposed is an SERR, defined exactly as in the case of incinerators.

Two examples will illustrate these ratings.

Efficiency of Pollution Control Devices

Other Pollution Control Devices (continued)

Example 1 - Assume that a catalytic cracker regenerator effluent contains 100 pounds of catalyst dust, 200 lbs. of carbon monoxide and 10 pounds of sulfur oxides per unit time. It is passed through a cyclone separator where 95 pounds of catalyst are removed. Therefore,

$$SE = \frac{100 - 5}{100} \times 100 = 95\%$$

$$\text{and } SERR = \frac{(100 \times 60 + 10 \times 20 + 200 \times 1) - (5 \times 60 + 10 \times 20 + 200 \times 1)}{(100 \times 60 + 10 \times 20 + 200 \times 1)} \times 100$$

$$= \frac{6400 - 700}{6400} \times 100 = 89\%$$

Example 2 - Assume that an organic liquid scrubber is used to wash a stream containing 50 pounds of SO_2 per unit time. All but one pound of the SO_2 is removed but two pounds of the hydrocarbon evaporate into the vented stream. Then

$$SE = \frac{50 - 1}{50} \times 100 = 98\%$$

$$\text{and } SERR = \frac{(50 \times 20) - (1 \times 20 + 2 \times 80)}{(50 \times 20)} \times 100$$

$$= \frac{1000 - 180}{1000} \times 100 = 82\%$$